

# Statistical Field Theory for Simple fluids : Mean Field and Gaussian Approximations

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We present an exact field theoretical representation of the statistical mechanics of simple classical liquids with short-ranged pairwise additive interactions. The action of the field theory is obtained by performing a Hubbard-Stratonovich transformation of the configurational Boltzmann factor. The mean field and Gaussian approximations of the theory are derived and applications to the liquid-vapour transition considered.

## I. INTRODUCTION

This article on a somehow new presentation of the theory of liquids is dedicated to D. Levesque at the occasion of his 65<sup>th</sup> birthday. Since Dominique and I share the same office, it was nearly impossible to keep secret the writing of the paper and I could not help myself discussing with him some parts of the manuscript. His deep knowledge of the theory of liquids made his remarks always pertinent and the final status of this article owes very much to our discussions.

The purpose of this work is to try to apply some of the techniques of statistical field theory to the physics of simple liquids. By "simple" we mean a liquid made of a single, chemically inert component which can be satisfactorily modelled by pairwise additive and spherically symmetric interactions<sup>1</sup>. More precisely we shall consider the case of a pair potential  $v(r)$  which can be written as the sum of a hard core interaction plus a short-ranged tail  $-w(r)$  which is supposed to decay faster than  $1/r^{3+\epsilon}$  at large  $r$  so that the thermodynamic limit exists<sup>1</sup>. Long-ranged electrostatic interactions are thus excluded of the present study as well as molecular liquids or mixtures. With the help of a Kac-Siegert-Stratonovich-Hubbard-Edwards (KSSHE)<sup>2-6</sup> transformation it is formally possible to reexpress the grand partition function of this system of decorated hard spheres as the grand partition function of bare hard spheres in an external stochastic potential or "field"  $\phi$  with a Gaussian measure<sup>3,7-10</sup>. We can thus describe the fluid with the help of a field theory characterised by an action  $\mathcal{H}(\phi)$  which however is quite complicated since, besides a simple quadratic term, it also includes the grand potential of the hard spheres which is a non local functional of the field  $\phi$ . Quite immodestly we however assume that this functional is perfectly known. Of course, it would be more satisfactory to treat the hard sphere interactions at the same level as the tail  $w(r)$  but the KSSHE transform requires a well behaved interaction (namely its Fourier transform must exist and be well behaved, see e.g. the appendix) and, unfortunately, hard core or more realistic less singular repulsive short-ranged potentials do not fulfill these mathematical requirements.

All the sophisticated techniques developed in statistical field theory<sup>11-14</sup> can thus be applied *a priori* to the case of liquids. Feynman graphs are no more difficult to compute than Mayer graphs which makes possible to perform effectively perturbative expansions of various thermodynamic quantities attached to the liquid in the KSSHE representation. Recently this type of approach was used to rediscover the low fugacity<sup>9,10</sup> and high temperature<sup>10</sup> expansions of the free energy and the equation of state of the restricted primitive model of electrolytes (RPM), results which had been obtained years ago before by awkward graph resummation techniques<sup>15,16</sup>.

Another powerful technique of statistical field theory is the so-called loop expansion which amounts to expand functionally the action  $\mathcal{H}(\phi)$  around a saddle-point<sup>12-14</sup>. The lowest order (zero loop) of the expansion, defines the mean field (MF) level of the theory. The MF theory of liquids in the KSSHE representation has been studied recently by Brilliantov et al. both for homogeneous liquids<sup>7</sup> and for liquids inhomogeneous in one direction of space<sup>8</sup>. In the former case, it yields to a van de Waals like theory of the liquid-vapour transition and, in the latter one, it allows the calculation of the MF surface tension. In the present paper we reconsider and extend Brilliantov's work on the MF level of the KSSHE theory and go a step further by considering also the one-loop approximation of the theory or,

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more precisely, a simplified version of it, called the Gaussian approximation in the literature<sup>11</sup>. In the homogeneous case it is shown to be strictly equivalent to the random phase approximation (RPA) of the theory of liquids<sup>1</sup>. The present work is hopefully a first step forwards a renormalized theory of the critical points of liquids at the one-loop order.

Our paper is organised as follows. In section II we expose in details some important properties of the KSSHE transform and establish notably the relation between the correlation functions of the fields and that of the fluctuations of densities. In section III the general MF equations of the KSSHE field theory are derived and their properties studied in details. As a subproduct of this formalism we obtain exact bounds for the free energy and the grand potential functionals. In next section IV the Gaussian approximation is derived and shown to be equivalent the RPA theory. In section V we reexpress the action  $\mathcal{H}(\phi)$  under a form similar to that of the Landau-Ginzburg (LG) Hamiltonian of magnetic systems which allows us to map the liquid-gas transition on the ferromagnetic one. In this way one can identify clearly the order parameter of the liquid-vapour transition which is, at least at the MF level, nothing but the density of the fluid, which rules out the field-mixing hypothesis<sup>17,18</sup>. In section VI the MF and Gaussian approximations are used to study in details the critical point of the fluid. We conclude in section VII.

## II. THE KSSHE TRANSFORM

### A. The KSSHE Transform of The Boltzmann Factor

We consider the case of a simple three dimensional fluid made of  $N$  identical hard spheres of diameter  $\sigma$  with additional pair interactions denoted for convenience  $-w(i, j)$ . Since  $w(i, j)$  is an arbitrary function in the core, i.e. for  $r_{ij} < \sigma$ , it is always possible to introduce the following decomposition :

$$\begin{aligned} w(i, j) &= w_-(i, j) - w_+(i, j) , \\ \tilde{w}_\pm(k) &= \int d^3\vec{r} \exp(i\vec{k}\cdot\vec{r}) w_\pm(r) > 0 \quad (\forall k) . \end{aligned} \quad (2.1)$$

In order to define safely the KSSHE transformation it is crucial to assume that the Fourier transforms of the pair potentials  $w_\pm(r)$  do exist and are both positive functions of  $k$  (for more details see the appendix). Moreover we demand  $\tilde{w}_\pm(k=0)$  and  $w_\pm(r=0)$  to be both well-behaved (finite) quantities. Clearly  $w_+(r)$  is the repulsive part of the tail and  $w_-(r)$  its attractive part.

Obviously the decomposition (2.1) is not unique, with the unpleasant consequence that approximate theories can depend upon the peculiar choice made for  $w_\pm(r)$  inside the core. We must precise however what we mean by an "approximate theory". If we mean a systematic expansion of some physical quantity in powers of some small physical parameter then the "theory" should be independant of the decomposition (2.1). This point was scrupulously considered in ref.<sup>10</sup> where it was shown that each term of the high-temperature and low activity expansions of the equation of state of the RPM obtained in the framework of the KSSHE formalism were indeed independant of the regularisation of the Coulomb potential inside the core.

By contrast, the small parameter of the loop-expansion considered in the present work is quite mysterious (we could have noted it  $\hbar$  according to the tradition !) and certainly not related to any physical parameter of the system<sup>12-14</sup>. As a consequence, each term of the expansion of the free energy of the liquid given in the following sections depends explicitly upon the regularisation of  $w(r)$  at short distances. We shall explain later on how to deal with, and even take advantage of the explicit dependance of the theory upon the decomposition (2.1) inside the core.

We denote by  $\Omega$  the domain of volume  $V$  occupied by the molecules of the fluid and by  $T$  their temperature. It is convenient to assume that  $\Omega$  is a cube with periodic boundary conditions (PBC). In a given configuration  $\omega = (N; \vec{r}_1 \dots \vec{r}_N)$  the microscopic density of particles reads

$$\hat{\rho}(\vec{r}|\omega) = \sum_{i=1}^N \delta^{(3)}(\vec{r} - \vec{r}_i) , \quad (2.2)$$

and the Boltzmann factor can thus be written

$$\exp(-\beta V(\omega)) = \exp(-\beta V_{HS}(\omega)) \exp(-N\nu_S) \exp\left(\frac{1}{2} \langle \hat{\rho} | \beta w | \hat{\rho} \rangle\right) , \quad (2.3)$$

where  $\beta = 1/k_B T$  ( $k_B$  Boltzmann factor) and  $\nu_S = \beta w(0)/2$  is minus the self-energy of the particles. From our hypothesis on  $w(r)$ ,  $\nu_S$  is a finite quantity which depends on the regularisation of the potential in the core. In eq.

(2.3)  $\exp(-\beta V_{HS}(\omega))$  denotes the hard sphere contribution to the Boltzmann factor and we have introduced the symbolic notation

$$\langle \hat{\rho} | w | \hat{\rho} \rangle \equiv \int_{\Omega} d^3 \vec{r}_1 d^3 \vec{r}_2 \hat{\rho}(\vec{r}_1 | \omega) w(\vec{r}_1, \vec{r}_2) \hat{\rho}(\vec{r}_2 | \omega) . \quad (2.4)$$

With our assumptions the two quadratic forms  $\langle \hat{\rho} | w_{\pm} | \hat{\rho} \rangle$  are both positive definite and we can take advantage of the properties of Gaussian functional integrals to rewrite

$$\begin{aligned} \exp \left( +\frac{1}{2} \langle \hat{\rho} | \beta w_- | \hat{\rho} \rangle \right) &= \langle \exp(\langle \hat{\rho} | \varphi_- \rangle) \rangle_{\beta w_-} \\ \exp \left( -\frac{1}{2} \langle \hat{\rho} | \beta w_+ | \hat{\rho} \rangle \right) &= \langle \exp(i \langle \hat{\rho} | \varphi_+ \rangle) \rangle_{\beta w_+} , \end{aligned} \quad (2.5)$$

where the scalar products  $\langle \hat{\rho} | \varphi_{\pm} \rangle$  of the microscopic density  $\hat{\rho}$  with the two real scalar fields  $\varphi_{\pm}(\vec{r})$  are defined as

$$\langle \hat{\rho} | \varphi_{\pm} \rangle = \int_{\Omega} d^3 \vec{r} \hat{\rho}(\vec{r} | \omega) \varphi_{\pm}(\vec{r}) . \quad (2.6)$$

The brackets  $\langle \dots \rangle_{\beta w_{\pm}}$  denote Gaussian averages over the fields  $\varphi_{\pm}(\vec{r})$  i.e.

$$\begin{aligned} \langle \dots \rangle_{\beta w_{\pm}} &\equiv \mathcal{N}_{\beta w_{\pm}}^{-1} \int \mathcal{D}\varphi_{\pm}(\vec{r}) \dots \exp \left( -\frac{1}{2} \langle \varphi_{\pm} | (\beta w_{\pm})^{-1} | \varphi_{\pm} \rangle \right) , \\ \mathcal{N}_{\beta w_{\pm}} &\equiv \int \mathcal{D}\varphi_{\pm}(\vec{r}) \exp \left( -\frac{1}{2} \langle \varphi_{\pm} | (\beta w_{\pm})^{-1} | \varphi_{\pm} \rangle \right) , \end{aligned} \quad (2.7)$$

where the inverse of  $\beta w_{\pm}$  must be understood in the sense of operators, i.e.

$$\int_{\Omega} d^3 \vec{r}_3 w_{\pm}(\vec{r}_1, \vec{r}_3) w_{\pm}^{-1}(\vec{r}_3, \vec{r}_2) = \delta^{(3)}(\vec{r}_1, \vec{r}_2) . \quad (2.8)$$

One could object that the relations (2.5), (2.7) and (2.8) are rather formal but in simple cases - i.e. if PBC are assumed - explicit and unambiguous expressions of the measure  $\mathcal{D}\varphi_{\pm}(\vec{r})$  can be given. See appendix A for more details. In order to simplify the notations further, we introduce the complex field  $\varphi(\vec{r}) \equiv \varphi_-(\vec{r}) + i\varphi_+(\vec{r})$ , define the measure

$$\mathcal{D}\varphi(\vec{r}) \equiv \mathcal{D}\varphi_+(\vec{r}) \mathcal{D}\varphi_-(\vec{r}) , \quad (2.9)$$

and the Gaussian average

$$\langle \dots \rangle_{\beta w} \equiv \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\varphi(\vec{r}) \dots \exp \left( -\frac{1}{2} \sum_{\epsilon=\pm} \langle \varphi_{\epsilon} | (\beta w_{\epsilon})^{-1} | \varphi_{\epsilon} \rangle \right) , \quad (2.10)$$

where  $\mathcal{N}_{\beta w} \equiv \mathcal{N}_{\beta w_+} \times \mathcal{N}_{\beta w_-}$ . We can thus rewrite the Boltzmann factor (2.3) as

$$\exp(-\beta V(\omega)) = \exp(-\beta V_{HS}(\omega)) \exp(N\nu_S) \langle \exp(\langle \varphi | \hat{\rho} \rangle) \rangle_{\beta w} . \quad (2.11)$$

Admittedly these notations can be misleading but they can be fully justified, see the beginning of section V for a more detailed discussion. Eq. (2.11) defines the KSSHE transform of the Boltzmann factor.

## B. The Physical meaning of the auxilliary fields

We have seen in section II A that, in a given configuration  $\omega$ , the Boltzmann factor of the fluid can be written as the statistical field partition function

$$z(\omega) \equiv \exp \left( \frac{1}{2} \langle \hat{\rho} | \beta w | \hat{\rho} \rangle \right) = \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\varphi \exp(-h[\varphi]) , \quad (2.12)$$

where  $h[\varphi]$  is a Gaussian Hamiltonian which reads

$$h[\varphi] = \frac{1}{2} \sum_{\epsilon=\pm} \langle \varphi_\epsilon | (\beta w_\epsilon)^{-1} | \varphi_\epsilon \rangle - \langle \varphi_- | \hat{\rho} \rangle - i \langle \varphi_+ | \hat{\rho} \rangle . \quad (2.13)$$

The saddle point of  $h[\varphi]$  is defined by the set of equations

$$\left. \frac{\delta h}{\delta \varphi_-(\vec{r})} \right|_{\overline{\varphi}} = \left. \frac{\delta h}{\delta \varphi_+(\vec{r})} \right|_{\overline{\varphi}} = 0 \quad (2.14)$$

the solution of which is

$$\begin{aligned} \overline{\varphi}_+(\vec{r}_1) &= i\beta \int_{\Omega} d^3\vec{r}_2 w_+(\vec{r}_1, \vec{r}_2) \hat{\rho}(\vec{r}_2) , \\ &\equiv i\beta w_+(\vec{r}_1, \cdot) * \hat{\rho}(\cdot) , \\ \overline{\varphi}_-(\vec{r}_1) &= \beta w_-(\vec{r}_1, \cdot) * \hat{\rho}(\cdot) , \end{aligned} \quad (2.15)$$

where the symbol  $'*'$  denotes a convolution in space. Note that eqs (2.15) imply the compact formula

$$\overline{\varphi}(\vec{r}_1) = \beta w(\vec{r}_1, \cdot) * \hat{\rho}(\cdot) , \quad (2.16)$$

where  $\overline{\varphi}(\vec{r}) = \overline{\varphi}_-(\vec{r}) + i\overline{\varphi}_+(\vec{r})$ , or, more explicitly

$$\overline{\varphi}(\vec{r}) = \sum_{i=1}^N \beta w(\vec{r} - \vec{r}_i) . \quad (2.17)$$

Therefore, at the saddle point, the KSSHE field  $\overline{\varphi}(\vec{r})$  is simply minus the local potential energy at point  $\vec{r}$ . Moreover one notes that

$$h[\overline{\varphi}] = -\frac{1}{2} \langle \hat{\rho} | \beta w | \hat{\rho} \rangle . \quad (2.18)$$

i.e. the value of  $h$  at the saddle point  $h[\overline{\varphi}]$  coincides with the configurational energy. Let us make the change of variables  $\varphi_{\pm}(\vec{r}) = \overline{\varphi}_{\pm}(\vec{r}) + \delta\varphi_{\pm}(\vec{r})$ , one has obviously, as a consequence of the stationarity,

$$h[\varphi] = h[\overline{\varphi}] + \frac{1}{2} \sum_{\epsilon=\pm} \langle \delta\varphi_\epsilon | (\beta w_\epsilon)^{-1} | \delta\varphi_\epsilon \rangle \quad (2.19)$$

The positivity of both operators  $w_{\pm}^{-1}$  confirms that  $(\overline{\varphi}, h[\overline{\varphi}])$  is indeed a saddle point. For a more complicated Hamiltonian than  $h[\varphi]$ , the approximation consisting in truncating the corrections to the saddle point value  $h[\overline{\varphi}]$  at the Gaussian level is called the Gaussian approximation<sup>11,12</sup>. This approximation is obviously exact for  $z(\omega)$  because  $h[\varphi]$  is a quadratic form. Indeed a direct calculation shows that

$$z_G \equiv \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\delta\varphi(\vec{r}) \exp \left( -h[\overline{\varphi}] - \frac{1}{2} \sum_{\epsilon=\pm} \langle \delta\varphi_\epsilon | (\beta w_\epsilon)^{-1} | \delta\varphi_\epsilon \rangle \right) = \exp(-h[\overline{\varphi}]) \equiv z(\omega) . \quad (2.20)$$

Note that it follows from eq. (2.15) that  $\overline{\varphi}_+$  is imaginary whereas we assumed the reality of the field  $\varphi_+$ . The integrals on  $\delta\varphi_+$  in eq. (2.20) correspond therefore to a mere translation for the contour of integration.

### C. The KSSHE Transform of The Grand Partition Function

Henceforward we shall work in the grand canonical (GC) ensemble. We denote by  $\mu$  the chemical potential and by  $\psi(\vec{r})$  an external potential. The local chemical potential will be noted  $\nu(\vec{r}) = \beta(\mu - \psi(\vec{r}))$  and the GC partition function reads :

$$\Xi[\nu] = \sum_{N=0}^{\infty} \frac{1}{N!} \int_{\Omega} d1 \dots dN \exp(-\beta V(\omega)) \prod_{i=1}^N \exp(\nu(i)) , \quad (2.21)$$

where  $i \equiv \vec{r}_i$  and  $di \equiv d^3\vec{r}_i$ .  $\Xi$  can be symbolically rewritten as

$$\Xi[\nu] = \int d\mu(\omega) \exp(-\beta V(\omega)) \exp(\langle \nu | \hat{\rho} \rangle) . \quad (2.22)$$

With these notations averages will be obtained by the formula

$$\langle A(\omega) \rangle_{GC} \equiv \frac{\int d\mu(\omega) A(\omega) \exp(-\beta V(\omega)) \exp(\langle \nu | \hat{\rho} \rangle)}{\int d\mu(\omega) \exp(-\beta V(\omega)) \exp(\langle \nu | \hat{\rho} \rangle)} . \quad (2.23)$$

As well known,  $\Xi[\nu]$  is log-convex functional of  $\nu^{19-21}$ . Inserting the expression (2.11) in eq. (2.21) one obtains readily a result which seems to have been established for the first time by Siegert<sup>3</sup>, i.e.

$$\Xi[\nu] = \langle \Xi_{HS}[\bar{\nu}] \rangle_{\beta w} . \quad (2.24)$$

where  $\bar{\nu}(\vec{r}) = \nu(\vec{r}) - \nu_S + \varphi(\vec{r})$ . Eq (2.24) tells us that the grand partition function  $\Xi$  of a fluid of decorated hard spheres is equal to the mean value of the grand partition function  $\Xi_{HS}$  of bare hard spheres in the presence of an external stochastic field with a Gaussian weight.

To make some contact with statistical field theory we also introduce the effective Hamiltonian (or action)

$$\mathcal{H}[\varphi] = \frac{1}{2} \sum_{\epsilon=\pm} \langle \varphi_\epsilon | (\beta w_\epsilon)^{-1} | \varphi_\epsilon \rangle - \log \Xi_{HS}[\bar{\nu}] , \quad (2.25)$$

which allows us to write alternatively for  $\Xi$

$$\Xi[\nu] = \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\varphi(\vec{r}) \exp(-\mathcal{H}[\varphi]) . \quad (2.26)$$

It will be important in the sequel to distinguish carefully two types of statistical field averages, the already defined  $\langle \dots \rangle_{\beta w}$  and the  $\langle \dots \rangle_{\mathcal{H}}$  that we define as

$$\langle A[\varphi] \rangle_{\mathcal{H}} \equiv \frac{\int \mathcal{D}\varphi(\vec{r}) \exp(-\mathcal{H}[\varphi]) A[\varphi]}{\int \mathcal{D}\varphi(\vec{r}) \exp(-\mathcal{H}[\varphi])} . \quad (2.27)$$

With these definitions in mind one notes that for an arbitrary functional of field  $\mathcal{A}[\varphi]$  one has

$$\langle A[\varphi] \rangle_{\mathcal{H}} = \frac{\langle A[\varphi] \Xi_{HS}[\bar{\nu}] \rangle_{\beta w}}{\langle \Xi_{HS}[\bar{\nu}] \rangle_{\beta w}} . \quad (2.28)$$

#### D. Preliminary Results on Correlation Functions.

The ordinary and connected correlation functions of the fluid will be defined in this paper as<sup>1,22,23</sup>

$$\begin{aligned} G^{(n)}[\nu](1, \dots, n) &= \frac{1}{\Xi[\nu]} \frac{\delta^n \Xi[\nu]}{\delta \nu(1) \dots \delta \nu(n)} , \\ &= \left\langle \prod_{i=1}^n \hat{\rho}(\vec{r}_i | \omega) \right\rangle_{GC} , \\ G_c^{(n)}[\nu](1, \dots, n) &= \frac{\delta^n \log \Xi[\nu]}{\delta \nu(1) \dots \delta \nu(n)} . \end{aligned} \quad (2.29)$$

Our notation emphasizes the fact that the  $G^{(n)}$  (connected and not connected) are functionals of the local chemical potential  $\nu(\vec{r})$  and functions of the coordinates  $(1, \dots, n) \equiv (\vec{r}_1, \dots, \vec{r}_n)$ . We know from the theory of liquids that<sup>22,23</sup>

$$G_c^{(n)}[\nu](1, \dots, n) = G^{(n)}[\nu](1, \dots, n) - \sum_{m < n} \prod_{i_1, \dots, i_m} G_c^{(m)}[\nu](i_1, \dots, i_m) , \quad (2.30)$$

where the sum of products is carried out over all possible partitions of the set  $(1, \dots, n)$  into subsets of cardinal  $m < n$ . In standard textbooks<sup>1</sup> the n-body correlations are usually defined as functional derivatives with respect to

the activity rather than with respect to the chemical potential. It yields to differences involving delta functions. For instance for  $n = 2$  and for a homogeneous system one has

$$\begin{aligned} G^{(2)}[\nu](1, 2) &= \rho^2 g(r_{12}) + \rho \delta(1, 2) , \\ G_c^{(2)}[\nu](1, 2) &= \rho^2 h(r_{12}) + \rho \delta(1, 2) , \end{aligned} \quad (2.31)$$

where  $\rho$  is the density of the fluid and  $g(r)$  the usual pair distribution function at chemical potential  $\nu$ , finally  $h = g - 1$ .

Of course we would like to relate the correlation functions of the microscopic density  $\hat{\rho}$  with the correlation functions of the KSSHE field  $\varphi$  defined as

$$\begin{aligned} G_\varphi^{(n)}[\nu](1, \dots, n) &= \left\langle \prod_{i=1}^n \varphi(i) \right\rangle_{\mathcal{H}} , \\ G_{\varphi,c}^{(n)}[\nu](1, \dots, n) &= G_\varphi^{(n)}[\nu](1, \dots, n) - \sum_{m < n} \prod_{i=1}^m G_{\varphi,c}^{(m)}[\nu](i_1, \dots, i_m) , \end{aligned} \quad (2.32)$$

From the expression (2.26) of  $\Xi$  and the definition (2.29) of  $G^{(n)}$  one infers that

$$G^{(n)}[\nu](1, \dots, n) = \Xi^{-1} \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\varphi \exp \left( -\frac{1}{2} \sum_{\epsilon=\pm} \langle \varphi_\epsilon | (\beta w_\epsilon)^{-1} | \varphi_\epsilon \rangle \right) \Xi_{HS}(\bar{\nu}) G_{HS}^{(n)}[\bar{\nu}](1, \dots, n) , \quad (2.33)$$

which yields, with the help of eq. (2.28), to the simple relation

$$G^{(n)}[\nu](1, \dots, n) = \left\langle G_{HS}^{(n)}[\bar{\nu}](1, \dots, n) \right\rangle_{\mathcal{H}} . \quad (2.34)$$

We are only half the way since the hard sphere correlation functions  $G_{HS}^{(n)}[\bar{\nu}]$  are of course complicated functionals of  $\varphi$  (through their dependence upon  $\bar{\nu}$ ). Let us first examine the simple case  $n = 1$  ( $G^{(n=1)} \equiv \rho$ ). We first rewrite eq. (2.34) for  $n = 1$  as

$$\begin{aligned} \rho[\nu](1) &= \langle \rho_{HS}[\bar{\nu}](1) \rangle_{\mathcal{H}} , \\ &= \Xi^{-1} \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\varphi \exp \left( -\frac{1}{2} \sum_{\epsilon=\pm} \langle \varphi_\epsilon | (\beta w_\epsilon)^{-1} | \varphi_\epsilon \rangle \right) \frac{\delta \Xi_{HS}(\bar{\nu})}{\delta \nu(1)} . \end{aligned} \quad (2.35)$$

Then one remarks that

$$\frac{\delta \Xi_{HS}(\bar{\nu})}{\delta \nu(1)} = \frac{\delta \Xi_{HS}(\bar{\nu})}{\delta \varphi_-(1)} = -i \frac{\delta \Xi_{HS}(\bar{\nu})}{\delta \varphi_+(1)} , \quad (2.36)$$

which allows us to replace the functional derivative of  $\Xi_{HS}$  with respect to  $\nu$  in the r.h.s of eq. (2.35) by a derivative either with respect to  $\varphi_-$  or with respect to  $\varphi_+$ . Let us do it in details in the former case. Since for functional integrals one has<sup>12</sup>

$$\int \mathcal{D}\varphi(\vec{r}) \frac{\delta I[\varphi]}{\delta \varphi_\pm(\vec{r})} = 0 , \quad (2.37)$$

An integration by parts yields the results

$$\begin{aligned} \rho[\nu](1) &= -\Xi^{-1} \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\varphi \frac{\delta \exp \left( -\frac{1}{2} \sum_{\epsilon=\pm} \langle \varphi_\epsilon | (\beta w_\epsilon)^{-1} | \varphi_\epsilon \rangle \right)}{\delta \varphi_-(1)} \Xi_{HS}(\bar{\nu}) , \\ &= (\beta w_-)^{-1}(1, \cdot) * \langle \varphi_-(\cdot) \rangle_{\mathcal{H}} . \end{aligned} \quad (2.38)$$

Repeating the above derivation with the field  $\varphi_+$  instead of  $\varphi_-$  and making use of the compact notations previously defined one finally arrives at the set of relations

$$\langle \varphi_-(1) \rangle_{\mathcal{H}} = \beta w_-(1, \cdot) * \langle \rho_{HS}[\bar{\nu}](\cdot) \rangle_{\mathcal{H}} , \quad (2.39a)$$

$$\langle \varphi_+(1) \rangle_{\mathcal{H}} = i \beta w_+(1, \cdot) * \langle \rho_{HS}[\bar{\nu}](\cdot) \rangle_{\mathcal{H}} , \quad (2.39b)$$

$$\langle \varphi(1) \rangle_{\mathcal{H}} = \beta w(1, \cdot) * \langle \rho_{HS}[\overline{\nu}](\cdot) \rangle_{\mathcal{H}} . \quad (2.39c)$$

For a homogeneous system one therefore has  $\langle \varphi \rangle_{\mathcal{H}} = \beta \tilde{w}(0) \rho$ . It can be noticed that eq. (2.39c) is analogous to a relation derived by Callen for an array of spins  $S_i$ <sup>24</sup>, namely  $\langle S_i \rangle = \langle \tanh(\beta h_i + \beta J_{ij} S_j) \rangle$  ( $h_i$  magnetic field on the site  $i$ ,  $J_{ik}$  coupling constant between sites  $i$  and  $j$ ). Callen's exact relation can be used to obtain the MF equations of spin systems by neglecting all correlations, which yields the well-known MF equations  $\overline{S}_i = \tanh(\beta h_i + \beta J_{ij} \overline{S}_j)$  where  $\overline{S}_i$  is the MF magnetisation of site  $i$ . Proceeding in an analogous way with eq (2.39c) one obtains the MF equations for the KSSHE field  $\varphi$ :

$$\overline{\varphi}(1) = \beta w(1, \cdot) * \rho_{HS}[\nu - \nu_S + \overline{\varphi}](\cdot) , \quad (2.40)$$

which will be derived more rigorously in next section.

This method of functional integration by parts can be used *a priori* at all orders so that to derive relations between the correlations  $G_{\varphi}^{(n)}$  of the field  $\varphi$  and the correlations  $G^{(n)}$  of the microscopic density  $\hat{\rho}$ . We just quote the result for  $n = 2$ .

$$\begin{aligned} G_{\varphi}^{(2)}[\nu](1, 2) &= \beta w(1, 2) + \beta w(1, \cdot) * G^{(2)}[\nu](\cdot, \cdot) * \beta w(\cdot, 2) , \\ G_{\varphi, c}^{(2)}[\nu](1, 2) &= \beta w(1, 2) + \beta w(1, \cdot) * G_c^{(2)}[\nu](\cdot, \cdot) * \beta w(\cdot, 2) . \end{aligned} \quad (2.41)$$

We leave the derivation of eqs. (2.41) by the method of integration by parts as an exercise for the reader. The result will be rederived and generalised to the case  $n \geq 3$  by a more elegant method in section V.

### III. MEAN FIELD THEORY

#### A. The grand-canonical free energy

We define the MF theory or saddle point approximation by the equation

$$\Xi_{MF}(\nu) \equiv \exp(-\mathcal{H}(\overline{\varphi})) , \quad (3.1)$$

where at  $\varphi = \overline{\varphi}$  the action  $\mathcal{H}$  is minimum. If there are several local minima then one retains the absolute minimum. The stationary condition reads

$$\left. \frac{\delta \mathcal{H}}{\delta \varphi_{\epsilon}(\vec{r})} \right|_{\overline{\varphi}} = 0 \quad (\epsilon = \pm) . \quad (3.2)$$

It follows readily from the expression (2.25) of  $\mathcal{H}$  that these eqs. may be written

$$\begin{aligned} \overline{\varphi}_-(1) &= \beta w_-(1, \cdot) * \rho_{HS}[\overline{\nu}](\cdot) , \\ \overline{\varphi}_+(1) &= i \beta w_+(1, \cdot) * \rho_{HS}[\overline{\nu}](\cdot) . \end{aligned} \quad (3.3)$$

By combining linearly eqs. (3.3) one recovers the MF eq. (2.40) for  $\varphi$ . The similarity between the MF eqs. (3.3) and (2.40) in one hand, and that which give the saddle point of  $h[\phi]$  in a given configuration of the phase space (cf. eqs. (2.15)) on the other hand, is striking although expected.

Making use of eqs (3.3) it is then easy to show that

$$\log \Xi_{MF}[\nu] = \log \Xi_{HS}[\overline{\nu}] - \frac{1}{2} \langle \rho_{HS}[\overline{\nu}] | \beta w | \rho_{HS}[\overline{\nu}] \rangle . \quad (3.4)$$

The MF density at point  $\vec{r}_1$  is obtained by taking the functional derivative of  $\log \Xi_{MF}[\nu]$  with respect to  $\nu(1)$ . It yields

$$\begin{aligned} \rho_{MF}[\nu](1) &= \frac{\delta \log \Xi_{MF}[\nu]}{\delta \nu(1)} \\ &= \rho_{HS}[\overline{\nu}](1) + \left\langle \rho_{HS}[\overline{\nu}] \left| \frac{\delta \overline{\varphi}}{\delta \nu(1)} - \beta w * \frac{\rho_{HS}}{\delta \nu(1)} \right. \right\rangle . \end{aligned} \quad (3.5)$$

The scalar product in the r.h.s of eq. (3.5) vanishes as a consequence of the stationarity conditions (3.2) and, finally, one finds

$$\rho_{MF}[\nu](1) = \rho_{HS}[\bar{\nu}](1) \quad (3.6)$$

We are now in position to compute the MF grand-canonical (MFGC) free energy as the Legendre Transform of  $\log \Xi_{MF}[\nu]$  with respect to the local chemical potential  $\nu(\vec{r})$

$$\beta \mathcal{A}_{MF}[\rho_{MF}] = \langle \rho_{MF} | \nu \rangle - \log \Xi_{MF}[\nu] \quad (3.7)$$

One finds after simple algebra that  $\mathcal{A}[\rho]$ , as a functional of  $\rho$ , can be expressed as

$$\beta \mathcal{A}_{MF}[\rho] = \beta \mathcal{A}_{HS}[\rho] + \int_{\Omega} d^3 \vec{r} \nu_S \rho(\vec{r}) - \frac{1}{2} \langle \rho | \beta w | \rho \rangle , \quad (3.8)$$

where  $\mathcal{A}_{HS}[\rho]$  is the exact GC free energy functional of the hard spheres at the density  $\rho$ . For a homogeneous system  $\mathcal{A}_{MF}(\rho)$  is merely the MF free energy of the system in the GC ensemble.

## B. The Mean Field Density Functionals

We recall first some important properties of the functionals  $\log \Xi[\nu]$  and  $\mathcal{A}[\rho]$ . Under quite general conditions it can be shown that the logarithm of the exact grand-partition function  $\log \Xi[\nu]$  is a convex functional of the local chemical potential  $\nu(\vec{r})$  and that the exact GC free energy  $\mathcal{A}[\rho]$  is a convex functional of the density  $\rho(\vec{r})$ <sup>19–21</sup>. It must be stressed that, for a finite system,  $\mathcal{A}[\rho]$  differs from the *canonical* free energy  $\mathcal{A}_C[\rho]$  which is not a convex functional of  $\rho(\vec{r})$  notably in the two-phases region due to interfacial effects. Moreover  $\log \Xi[\nu]$  and  $\mathcal{A}[\rho]$  constitute a pair of Legendre transforms, an important property which can be expressed as

$$\beta \mathcal{A}[\rho] = \sup_{\nu \in \mathcal{U}} (\langle \rho | \nu \rangle - \log \Xi[\nu]) \quad (\forall \rho \in \mathcal{R}) , \quad (3.9)$$

$$\log \Xi[\nu] = \sup_{\rho \in \mathcal{R}} (\langle \rho | \nu \rangle - \beta \mathcal{A}[\rho]) \quad (\forall \nu \in \mathcal{U}) . \quad (3.10)$$

It can also be shown that the sets of physical densities  $\mathcal{R}$  and that of local chemical potentials  $\mathcal{U}$  are both convex sets<sup>19,21</sup>. The so-called Young inequalities follows directly from eqs (3.9), (3.10) and read

$$\beta \mathcal{A}[\rho] + \log \Xi[\nu] \geq \langle \rho | \nu \rangle \quad (\forall \rho \in \mathcal{R}, \forall \nu \in \mathcal{U}) . \quad (3.11)$$

Finally we recall that a necessary and sufficient condition for the convexity of  $\log \Xi[\nu]$  and  $\mathcal{A}[\rho]$  is that their second order functional derivatives are positive operators, i.e.<sup>19–21</sup>

$$\begin{aligned} \left\langle \delta \nu \left| \frac{\delta^{(2)} \log \Xi[\nu]}{\delta \nu(1) \delta \nu(2)} \right. \right\rangle & (\equiv G_c^{(2)}[\nu]) \delta \nu \geq 0 \quad (\forall \nu, \delta \nu \in \mathcal{U}) , \\ \left\langle \delta \rho \left| \frac{\delta^{(2)} \beta \mathcal{A}[\rho]}{\delta \rho(1) \delta \rho(2)} \right. \right\rangle & (\equiv -\hat{C}^{(2)}[\rho]) \delta \rho \geq 0 \quad (\forall \rho, \delta \rho \in \mathcal{R}) . \end{aligned} \quad (3.12)$$

Moreover the two-body direct correlation function  $\hat{C}^{(2)}[\rho]$  is minus the inverse of the connected two-body correlation function  $G_c^{(2)}[\nu]$  i.e.

$$G_c^{(2)}[\nu](1, \cdot) * \hat{C}^{(2)}[\rho](\cdot, 2) = -\delta(1, 2) \quad (3.13)$$

where it must be stressed that  $\nu[\rho]$  is the (unique) local chemical potential corresponding to the density profile  $\rho$ . We have now at our disposal all the mathematical tools necessary to prove the two following theorems

- if  $w_+ = 0$  (attractive case)  $\beta \mathcal{A}_{MF}[\rho]$  is an upper bound of  $\beta \mathcal{A}[\rho]$
- if  $w_- = 0$  (repulsive case)  $\beta \mathcal{A}_{MF}[\rho]$  is a lower bound of  $\beta \mathcal{A}[\rho]$



Let us consider first the attractive case ( $w_+ = 0$ ). We start with the fundamental relation (2.21) which reads in this case

$$\Xi[\nu] = \langle \exp(\log \Xi_{HS}[\nu - \nu_S + \varphi_-]) \rangle_{\beta w_-} \quad (\forall \nu \in \mathcal{U}) . \quad (3.14)$$

We now apply Young's inequalities (3.11) to  $\log \Xi_{HS}$  which yields

$$\begin{aligned} \Xi[\nu] &\geq \langle \exp(-\beta \mathcal{A}[\rho] + \langle \rho | \nu - \nu_S + \varphi_- \rangle) \rangle_{\beta w_-} \quad (\forall \nu \in \mathcal{U}, \forall \rho \in \mathcal{R}) \\ &\equiv \exp \left( -\beta \mathcal{A}_{HS}[\rho] + \langle \rho | \nu - \nu_S \rangle + \frac{1}{2} \langle \rho | \beta w_- | \rho \rangle \right) \quad (\forall \nu \in \mathcal{U}, \forall \rho \in \mathcal{R}) . \end{aligned} \quad (3.15)$$

where we have made use of the property (2.5) of Gaussian integrals. Taking the logarithm one arrives at

$$\beta \mathcal{A}_{MF}[\rho] \equiv \beta \mathcal{A}_{HS}[\rho] + \langle \rho | \nu_S \rangle - \frac{1}{2} \langle \rho | \beta w_- | \rho \rangle \geq \langle \rho | \nu \rangle - \log \Xi[\nu] ; \quad (\forall \nu \in \mathcal{U}, \forall \rho \in \mathcal{R}) . \quad (3.16)$$

which implies

$$\beta \mathcal{A}_{MF}[\rho] \geq \sup_{\nu \in \mathcal{U}} (\langle \rho | \nu \rangle - \log \Xi[\nu]) \equiv \beta \mathcal{A}[\rho] \quad (w_+ \equiv 0, \forall \rho \in \mathcal{R}) . \quad (3.17)$$

Good approximate functionals  $\beta \mathcal{A}_{HS}[\rho]$  are available in the literature for the hard sphere fluid. Our  $\beta \mathcal{A}_{MF}[\rho]$  could be of some use to deal with systems of decorated hard spheres. Note that  $\beta \mathcal{A}_{MF}[\rho]$  is also a functional of the pair potential  $\beta w_-(r)$  in the core ( $r \leq \sigma$ ); therefore an optimized version of the MFGC free energy can be obtained by minimizing  $\beta \mathcal{A}_{MF}[\rho]$  with respect to  $w_-(r)$  in the core.

The repulsive case ( $w_- = 0$ ) is more tricky. One first remarks that, in this case, one has

$$\Xi[\nu] = \langle \exp(\log \Xi_{HS}[\nu - \nu_S + i\varphi_+]) \rangle_{\beta w_+} \quad (\forall \nu \in \mathcal{U}) . \quad (3.18)$$

which implies

$$\Xi_{HS}[\nu] = \langle \exp(\log \Xi[\nu + \nu_S + \varphi_+]) \rangle_{\beta w_+} \quad (\forall \nu \in \mathcal{U}) . \quad (3.19)$$

We are thus led back to the previous case. We therefore apply now Young's inequalities (3.11) to  $\log \Xi$  which yields

$$\Xi_{HS}[\nu] \geq \exp \left( -\beta \mathcal{A}[\rho] + \langle \rho | \nu + \nu_S \rangle + \frac{1}{2} \langle \rho | \beta w_+ | \rho \rangle \right) \quad (\forall \nu \in \mathcal{U}, \forall \rho \in \mathcal{R}) , \quad (3.20)$$

where we made use, once again of the fundamental property of Gaussian integrals (cf eq. (2.5)). Taking the logarithm we are thus led to the following inequalities

$$\beta \mathcal{A}[\rho] \geq -\log \Xi_{HS}[\nu] + \langle \rho | \nu + \nu_S \rangle - \frac{1}{2} \langle \rho | \beta w_+ | \rho \rangle \quad (\forall \nu \in \mathcal{U}, \forall \rho \in \mathcal{R}) , \quad (3.21)$$

where we have noted that, in the repulsive case,  $w_+ = -w_-$ . Since the inequality (3.21) is valid for any  $\nu \in \mathcal{U}$  for a given  $\rho \in \mathcal{R}$  it is also true for  $\nu^* = \sup \nu$  ( $\nu \in \mathcal{U}$ ) which yields the desired result

$$\beta \mathcal{A}[\rho] \geq \beta \mathcal{A}_{MF}[\rho] \quad (w_- \equiv 0, \forall \rho \in \mathcal{R}) . \quad (3.22)$$

In the repulsive case an optimized version of the MFGC free energy can thus be obtained by maximizing  $\beta \mathcal{A}_{MF}[\rho]$  with respect to  $w_+(r)$  in the core.

In the general case, i.e. when  $w = w_- - w_+$  ( $w_- \neq 0$  and  $w_+ \neq 0$ )  $\mathcal{A}_{MF}[\rho]$  is neither an upper or a lower bound for the exact GC free energy. Moreover, in the homogeneous case, there is no clear relation between  $\mathcal{A}_{MF}[\rho]$  and the Gibbs-Bogoliubov bounds<sup>1</sup> for the free energy.

### C. The Mean Field Correlation Functions

#### 1. The connected two-points correlation function

The MF connected two-points correlation function will be defined according to eq. (2.29), i.e. as

$$\begin{aligned}
G_{MF,c}^{(2)}[\nu](1,2) &= \frac{\delta^2 \log \Xi_{MF}[\nu]}{\delta \nu(1) \delta \nu(2)}, \\
&= \frac{\delta \rho_{MF}[\nu](2)}{\delta \nu(1)}.
\end{aligned} \tag{3.23}$$

Since  $\rho_{MF}[\nu](2) = \rho_{HS}[\nu - \nu_S + \bar{\varphi}](2)$  (cf. eq. (3.6)) the MF density  $\rho_{MF}[\nu]$  is a functional of the local chemical potential  $\nu$  directly and also through the KSSHE field  $\bar{\varphi}[\nu]$ . Therefore one has

$$G_{MF,c}^{(2)}[\nu](1,2) = G_{HS,c}^{(2)}[\bar{\nu}](1,2) + \int d3 G_{HS,c}^{(2)}[\bar{\nu}](1,3) \frac{\delta \bar{\varphi}(3)}{\delta \nu(2)}. \tag{3.24}$$

We note that it follows from the MF eq. (2.40) that

$$\frac{\delta \bar{\varphi}(3)}{\delta \nu(2)} = \beta w(3, \cdot) * G_{MF,c}^{(2)}[\nu](\cdot, 2) \tag{3.25}$$

from which we infer the relation

$$G_{MF,c}^{(2)}[\nu] = G_{HS,c}^{(2)}[\bar{\nu}] + G_{HS,c}^{(2)}[\bar{\nu}] * \beta w * G_{MF,c}^{(2)}[\nu] \tag{3.26}$$

which can be solved formally to give

$$G_{MF,c}^{(2)}[\nu] = (1 - \beta w * G_{HS,c}^{(2)}[\bar{\nu}])^{-1} * G_{HS,c}^{(2)}[\bar{\nu}]. \tag{3.27}$$

For a homogeneous system the Fourier transform of  $G_{MF,c}^{(2)}$  therefore reads as

$$\tilde{G}_{MF,c}^{(2)}[\nu](k) = \frac{\tilde{G}_{HS,c}^{(2)}[\bar{\nu}](k)}{1 - \beta \tilde{w}(k) \tilde{G}_{HS,c}^{(2)}[\bar{\nu}](k)}. \tag{3.28}$$

## 2. The direct two-points correlation function

The MF two-points direct correlation function will be defined according to eq. (3.12), i.e. as

$$\hat{C}_{MF}^{(2)}[\rho](1,2) = -\frac{\delta^2 \beta \mathcal{A}_{MF}[\rho]}{\delta \rho(1) \delta \rho(2)}. \tag{3.29}$$

In the terminology of statistical field theory  $\hat{C}_{MF}^{(2)}[\rho](1,2)$  is a vertex function, it is related to the usual direct correlation function  $c(1,2)$  by the relation  $\hat{C}_{MF}^{(2)}[\rho](1,2) = c_{MF}[\rho](1,2) - \delta(1,2)/\rho(1)^{22,23}$ . It readily follows from the expression (3.8) of the MFGC free energy that we have

$$\hat{C}_{MF}^{(2)}[\rho](1,2) = \hat{C}_{HS}^{(2)}[\rho](1,2) + \beta w(1,2). \tag{3.30}$$

Some remarks are at order. Firstly, it can be checked that the mean-field operators  $-\hat{C}_{MF}^{(2)}$  is indeed the inverse of  $G_{MF,c}^{(2)}$ ; more precisely one checks readily that, formally

$$\hat{C}_{MF}^{(2)}[\rho](1, \cdot) * G_{MF,c}^{(2)}[\nu](\cdot, 2) = -\delta(1,2), \tag{3.31}$$

where it must be stressed that in the above equation  $\rho$  denotes the mean-field density at the local chemical potential  $\nu$ , i.e.  $\rho \equiv \rho_{HS}[\bar{\nu}]$ . For a homogeneous system the Ornstein-Zernike (OZ) eq. (3.31) can be written simply in Fourier space as  $\tilde{G}_{MF,c}^{(2)}[\nu](k) \tilde{\hat{C}}_{MF,c}^{(2)}[\rho](k) = -1$ . Secondly it must be stressed that the expression (3.27) of the connected correlation function  $G_{MF,c}^{(2)}$  is rather formal. Its validity, and thus the validity of the OZ relation (3.31) as well, is guaranteed only if the inverse of the operator  $1 - \beta w * G_{HS,c}^{(2)}[\nu]$  does exist. It can be expected to be true only if  $T > T_c$  where  $T_c$  is the (mean field) critical temperature. Below  $T_c$  the first derivatives of the MF grand potential with respect to  $\nu$  have discontinuities at the chemical potential corresponding to the coexistence of the vapour and liquid phases and the second derivatives (i.e.  $G_{MF,c}^{(2)}[\nu]$ ) are not defined.

### 3. Rigorous bounds for Log $\Xi[\nu]$

It transpires from the above discussion that for  $T > T_c$  the MF correlation function  $G_{MF,c}^{(2)}[\nu]$  is a positive operator, i.e. that

$$(\forall \nu, \forall h \in \mathcal{U}) \quad \left\langle h | G_{MF,c}^{(2)}[\nu] | h \right\rangle \geq 0 . \quad (3.32)$$

It follows then from the OZ eq. (3.31) that for  $T > T_c$  and for all densities  $\rho \in \mathcal{R}$ ,  $\hat{C}_{MF,c}^{(2)}[\rho]$  is also a positive operator. Consequently, both  $\log \Xi_{MF}[\nu]$  and  $\beta \mathcal{A}_{MF}[\rho]$  are convex functional of respectively the generalised chemical potential  $\nu$  and the density  $\rho$ . Moreover they constitute a pair of Legendre transforms by construction and thus satisfy to the eqs. (3.9), (3.10). Exact bounds for  $\log \Xi[\nu]$ , valid for  $T > T_c$ , can be deduced from this property

Let us start with the case of a repulsive pair potential (i.e.  $w_- \equiv 0$ ). In this case  $\beta \mathcal{A}[\rho] \geq \beta \mathcal{A}_{MF}[\rho]$  for all  $\rho$  as shown by eq. (3.22). Therefore, for  $T > T_c$

$$\begin{aligned} \log \Xi_{MF}[\nu] &= \sup_{\rho \in \mathcal{R}} (\langle \rho | \nu \rangle - \beta \mathcal{A}_{MF}[\rho]) \quad (\forall \nu \in \mathcal{U}) , \\ &\geq \sup_{\rho \in \mathcal{R}} (\langle \rho | \nu \rangle - \beta \mathcal{A}[\rho]) \quad (\forall \nu \in \mathcal{U}) , \end{aligned} \quad (3.33)$$

from which we conclude that

$$\log \Xi_{MF}[\nu] \geq \log \Xi[\nu] \quad (T > T_c, w_- \equiv 0, \forall \nu \in \mathcal{U}) . \quad (3.34)$$

In the case of a purely attractive pair potential (i.e.  $w_+ \equiv 0$ ) it can be shown similarly that

$$\log \Xi_{MF}[\nu] \leq \log \Xi[\nu] \quad (T > T_c, w_+ \equiv 0, \forall \nu \in \mathcal{U}) . \quad (3.35)$$

## IV. THE GAUSSIAN APPROXIMATION

### A. The grand potential

Let us define the Gaussian approximation of the KSSHE field theory in the following way<sup>11</sup>. First we write

$$\begin{aligned} \varphi_- &= \bar{\varphi}_- + \xi_- , \\ \varphi_+ &= \bar{\varphi}_+ + \xi_+ , \end{aligned} \quad (4.1)$$

where  $\xi_-$  and  $\xi_+$  are real scalar fields ( $\xi$  will be defined as  $\xi = \xi_- + i\xi_+$ ) and then we expand functionally the action  $\mathcal{H}[\varphi]$  (cf eq. (2.25)) up to second order in  $\xi_{\pm}$  around the MF solution. In this way the exact action  $\mathcal{H}[\varphi]$  is replaced by an approximate action  $\mathcal{H}_G[\varphi]$  defined symbolically as

$$\mathcal{H}_G[\varphi] = \mathcal{H}[\bar{\varphi}] + \frac{1}{2} \int_{\Omega} d(1) d(2) \left. \frac{\delta^2 \mathcal{H}}{\delta \varphi(1) \delta \varphi(2)} \right|_{\bar{\varphi}} \xi(1) \xi(2) . \quad (4.2)$$

Note that the terms linear in  $\xi$  are absent from eq. (4.2) as a consequence of the stationarity condition (3.2). Taking into account the explicit expression (2.25) of  $\mathcal{H}$  we have more precisely

$$\mathcal{H}_G[\varphi] = \mathcal{H}[\bar{\varphi}] + \frac{1}{2} \sum_{\epsilon=\pm} \langle \xi_{\epsilon} | \Delta_{\epsilon}^{-1} | \xi_{\epsilon} \rangle - i \left\langle \xi_+ | G_{HS,c}^{(2)}[\bar{\nu}] | \xi_- \right\rangle , \quad (4.3)$$

where the operators  $\Delta_{\pm}$  are functionals of  $\bar{\nu} = \nu - \nu_S + \bar{\varphi}$  and are defined as

$$\Delta_{\pm}^{-1} \equiv (\beta w_{\pm})^{-1} \pm G_{HS,c}^{(2)}[\bar{\nu}] . \quad (4.4)$$

or equivalently

$$\Delta_{\pm} = \beta w_{\pm} * (1 \pm G_{HS,c}^{(2)}[\bar{\nu}] * \beta w_{\pm})^{-1} . \quad (4.5)$$

Clearly the Gaussian approximation makes sense only if both operators  $\Delta_{\pm}$  are positive, which will be assumed henceforth.

The Gaussian grand partition function is obtained by replacing  $\mathcal{H}[\varphi]$  by its Gaussian approximation  $\mathcal{H}_G[\varphi]$  in the expression (2.26) of  $\Xi[\nu]$ , which gives

$$\Xi_G[\nu] = \exp(-\mathcal{H}[\bar{\varphi}]) \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\xi_+ \mathcal{D}\xi_- \exp\left(-\frac{1}{2} \sum_{\epsilon=\pm} \langle \xi_{\epsilon} | \Delta_{\epsilon}^{-1} | \xi_{\epsilon} \rangle + i \langle \xi_+ | G_{HS,c}^{(2)}[\bar{\nu}] | \xi_- \rangle\right) \quad (4.6)$$

$\Xi_G[\nu]$  can be explicitly computed in the case of a homogeneous system. For instance, by first performing the Gaussian integrals on the variable  $\xi_+$  then on  $\xi_-$ , one easily obtains that

$$\Xi_G[\nu] = \exp(-\mathcal{H}[\bar{\varphi}]) \mathcal{N}_{\beta w}^{-1} \mathcal{N}_{\Delta_+} \mathcal{N}_{X_-} , \quad (4.7)$$

or, by reverting the order of integrations on  $\xi_+$  and  $\xi_-$ , that

$$\Xi_G[\nu] = \exp(-\mathcal{H}[\bar{\varphi}]) \mathcal{N}_{\beta w}^{-1} \mathcal{N}_{\Delta_-} \mathcal{N}_{X_+} . \quad (4.8)$$

The operators  $X_{\pm}$  which enters eqs. (4.7,4.8) being defined by the relations

$$X_{\pm}^{-1} = \Delta_{\pm}^{-1} + G_{HS,c}^{(2)}[\bar{\nu}] * \Delta_{\mp} * G_{HS,c}^{(2)}[\bar{\nu}] . \quad (4.9)$$

Since  $\mathcal{N}_{\beta w} = \mathcal{N}_{\beta w_+} \mathcal{N}_{\beta w_-}$  we see that only ratios of the normalization constants  $\mathcal{N}$  of various operators enter the expressions (4.7, 4.8) of  $\Xi_G[\nu]$ . These ratios are easily evaluated with the help the eq. (A12) of appendix A. For  $\log \Xi \equiv V\beta P$  holds for a homogeneous system, one obtains finally for the pressure  $P_G$

$$\begin{aligned} \beta P_G(\nu) &= \beta P_{MF}(\nu) + \frac{1}{2} \int \frac{d^3 \vec{k}}{(2\pi)^3} \log \left( \frac{\tilde{\Delta}_-(k) \tilde{X}_+(k)}{\beta \tilde{w}_+(k) \beta \tilde{w}_-(k)} \right) \\ &= \beta P_{HS}(\bar{\nu}) - \frac{1}{2} \beta \tilde{w}(0) \rho_{HS}^2(\bar{\nu}) + \frac{1}{2} \int \frac{d^3 \vec{k}}{(2\pi)^3} \log \left( 1 - \tilde{w}(k) \tilde{G}_{HS,c}^{(2)}[\bar{\nu}](k) \right) . \end{aligned} \quad (4.10)$$

## B. The correlation functions and the free energy

The mean values of the type (2.28) with the full action  $\mathcal{H}$  replaced by its Gaussian approximation  $\mathcal{H}_G$  will be denoted by  $\langle \dots \rangle_G$ . Clearly one has  $\langle \xi_{\pm} \rangle_G = 0$  from which we infer that

$$\rho_G[\nu] = \rho_{MF}[\nu] = \rho_{HS}[\bar{\nu}] . \quad (4.11)$$

The various pair correlations of the KSSHE fields  $\varphi_{\pm}$  are obtained by applying Wick's theorem (cf eq. (A14)) with the result

$$\langle \varphi_{\pm}(1) \varphi_{\pm}(2) \rangle_{G,c} = X_{\pm}(1, 2) , \quad (4.12a)$$

$$\langle \varphi_+(1) \varphi_-(2) \rangle_{G,c} = i \Delta_+(1, \cdot) * G_{HS,c}^{(2)}[\bar{\nu}](\cdot, \cdot) * \langle \varphi_-(\cdot) \varphi_-(2) \rangle_{G,c} . \quad (4.12b)$$

After some algebraic manipulations more easily effectuated in Fourier space, one obtains the more transparent relations

$$\langle \varphi_{\pm}(1) \varphi_{\pm}(2) \rangle_{G,c} = \beta w_{\pm}(1, 2) \mp \beta w_{\pm}(1, \cdot) * G_{MF,c}^{(2)}[\nu](\cdot, \cdot) * \beta w_{\pm}(\cdot, 2) , \quad (4.13a)$$

$$\langle \varphi_+(1) \varphi_-(2) \rangle_{G,c} = i \beta w_+(1, \cdot) * G_{MF,c}^{(2)}[\nu](\cdot, \cdot) * \beta w_-(\cdot, 2) , \quad (4.13b)$$

$$\langle \varphi(1) \varphi(2) \rangle_{G,c} = \beta w(1, 2) + \beta w(1, \cdot) * G_{MF,c}^{(2)}[\nu](\cdot, \cdot) * \beta w(\cdot, 2) . \quad (4.13c)$$

The comparison of these formula with eqs. (2.41) shows that  $G_{MF}^{(2)} \equiv G_G^{(2)}$  a well known property of the Gaussian approximation<sup>11</sup>. Recall however that we have defined  $G_{MF}^{(2)}$  as the second functional derivative of  $\Xi_{MF}[\nu]$  with respect to  $\nu$ . The second functional derivative of  $\Xi_G[\nu]$  with respect to  $\nu$  differs of  $G_G^{(2)}$  as defined above by terms involving the three-body correlation function of the HS reference fluid. This difference between the two possible definitions of

$G_G^{(2)}$  coincides in fact with the so-called one-loop correction to  $G_G^{(2)}$  which play an important role in the renormalized theory of the critical point (such a theory remains however to be worked out explicitly !). The previous remarks could be extended to all correlation functions; for instance at the one-loop order the density does not coincides with the MF or Gaussian result.

Since  $\rho_G = \rho_{MF}$  the Legendre transform of  $\log \Xi_G[\nu]$ , i.e. the free energy of a homogeneous system in the Gaussian approximation is easily derived. Let  $f_G \equiv \mathcal{A}_G/V$  be the specific free energy; we have

$$\beta f_G(\rho) = \beta f_{MF}(\rho) + \beta \Delta f(\rho) , \quad (4.14a)$$

$$\beta f_{MF}(\rho) = \beta f_{HS}(\rho) - \frac{\beta}{2} \tilde{w}(0) \rho^2 + \frac{\beta}{2} \rho w(0) , \quad (4.14b)$$

$$\beta \Delta f(\rho) = \frac{1}{2} \int \frac{d^3 \vec{k}}{(2\pi)^3} \log \left( 1 - \beta \tilde{w}(k) \tilde{G}_{HS,c}^{(2)}[\rho](k) \right) . \quad (4.14c)$$

It should be noticed that the expressions derived above in the framework of the Gaussian approximation for the correlations  $\hat{C}_G^{(2)}$ , and  $G_{G,c}^{(2)}$ , and for the free ennergy  $f_G$  coincide with those obtained in the framework of the RPA theory of simple fluids<sup>1</sup>. As well known, the RPA theory becomes exact in the limit of an infinitely long-ranged interaction  $w(r) = \gamma^3 w_0(\gamma r)$ ,  $\gamma \rightarrow 0^1$ .

Note that, as in the case of the MF theory, the free energy (4.14) depends on the value of the pair potential  $w$  in the core, which is arbitrary. We can take advantage of this freedom of the theory by requiring the stationarity condition

$$\frac{\delta \beta f_G}{\delta \beta w(\vec{r})} \equiv 0 \text{ for } ||\vec{r}|| \leq \sigma . \quad (4.15)$$

For it is easy to derive from (4.14) that

$$\frac{\delta \beta f_G}{\delta \beta w(\vec{r})} = -\frac{\rho^2}{2} g_G(\vec{r}) ,$$

the stationarity condition (4.15) on  $\beta f_G$  implies the nullity of the radial pair distribution function in the core, an important physical requirement. This optimized Gaussian approximation coincides of course with the ORPA theory of the theory of liquids<sup>1</sup>.

## V. THE LANDAU-GINZBURG ACTION

We first note that, quite remarkably, all the results of the previous sections could have been obtained more simply by ignoring the complications introduced by the presence of two distinct KSSHE fields  $\varphi_+$  and  $\varphi_-$  associated with the repulsive and attractive part of the pair potential respectively, and by considering rather a unique KSSHE field  $\varphi$ . Indeed, taking as a starting point the simplified definitions

$$\Xi[\nu] = \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\varphi(\vec{r}) \exp(-\mathcal{H}[\varphi]) , \quad (5.1a)$$

$$\mathcal{H}[\varphi] = \frac{1}{2} \langle \varphi | (\beta w)^{-1} | \varphi \rangle - \log \Xi_{HS}[\overline{\nu}] , \quad (5.1b)$$

$$\mathcal{N}_{\beta w} = \int \mathcal{D}\varphi(\vec{r}) \exp \left( - \langle \varphi | (\beta w)^{-1} | \varphi \rangle \right) \quad (5.1c)$$

without any requirement on the positivity of the quadratic form  $\langle \varphi | (\beta w)^{-1} | \varphi \rangle$ , yields the MF and Gaussian expressions for the MF and Gaussian expressions for  $\log \Xi$ , the free energy and the correlation functions. This remark justifies *a posteriori* the notations (2.9) adopted at the beginning of section II A. Henceforth, in order to avoid any awkward complications in further developments we shall adopt definitively the somehow abusive definitions (5.1).

We show now that the action  $\mathcal{H}[\varphi]$  can be rewritten as the Landau-Ginzburg (LG) action of a magnetic system in the presence of a magnetic field  $B$ . Following Brilliantov<sup>7</sup> we make choice of a reference chemical potential  $\nu_0$  for the HS reference system (supposed to be uniform for simplicity and to be specified further) and perform a functional Taylor expansion of  $\log \Xi_{HS}$  around  $\nu_0$ . Let us first define for further convenience

$$\Delta \nu(\vec{r}) = \nu(\vec{r}) - \nu_S - \nu_0 , \quad (5.2a)$$

$$\phi(\vec{r}) = \Delta \nu(\vec{r}) + \varphi(\vec{r}) . \quad (5.2b)$$

With these definitions we have  $\overline{\nu} = \nu_0 + \phi$ . Now, assuming the analiticity of  $\log \Xi_{HS}$  at  $\nu_0$  we have, for  $\overline{\nu}$  in some neighborhood of  $\nu_0$

$$\log \Xi_{HS}[\overline{\nu}] = \log \Xi_{HS}[\nu_0] + \langle \phi | \rho_{HS}[\nu_0] \rangle + \frac{1}{2} \langle \phi | G_{HS,c}^{(2)}[\nu_0] | \phi \rangle - \mathcal{V}_I[\phi] , \quad (5.3a)$$

$$\mathcal{V}_I[\phi] = - \sum_{n=3}^{\infty} \frac{1}{n!} \int d1 \dots dn G_{HS,c}^{(n)}[\nu_0](1, \dots, n) \phi(1) \dots \phi(n) . \quad (5.3b)$$

Therefore one can rewrite the expression (2.25) of  $\Xi[\nu]$  as

$$\Xi[\nu] = \exp(-\overline{\mathcal{H}}) \Xi_{LG}[B] , \quad (5.4a)$$

$$\overline{\mathcal{H}} = \frac{1}{2} \langle \Delta \nu | (\beta w)^{-1} | \Delta \nu \rangle - \log \Xi_{HS}[\nu_0] , \quad (5.4b)$$

where  $\overline{\mathcal{H}}$  is a simple Gaussian functional of  $\nu$  and  $\Xi_{LG}[B]$  may be seen as the partition function of a LG model in the presence of a magnetic field  $B$ . Indeed

$$\Xi_{LG}[B] = \mathcal{N}_{\beta w}^{-1} \int \mathcal{D}\phi(\vec{r}) \exp(-\mathcal{H}_{LG,0}[\phi] + \langle B | \phi \rangle) , \quad (5.5a)$$

$$\mathcal{H}_{LG,0}[\phi] = \frac{1}{2} \langle \phi | \Delta^{-1} | \phi \rangle + \mathcal{V}_I[\phi] , \quad (5.5b)$$

where the free propagator of the theory  $\Delta$  is given by  $\Delta^{-1} = (\beta w)^{-1} - G_{HS,c}^{(2)}[\nu_0]$  or equivalently

$$\Delta = \beta w * (1 - \beta w * G_{HS,c}^{(2)}[\nu_0])^{-1} , \quad (5.6)$$

and the magnetic field  $B$  by

$$B = \rho_{HS}[\nu_0] + (\beta w)^{-1} * \Delta \nu . \quad (5.7)$$

It can be noticed that the interaction term  $\mathcal{V}_I[\phi]$  of the LG action  $\mathcal{H}_{LG,0}$  is non local and does not exhibit the usual symetry  $\mathcal{V}_I[\phi] = \mathcal{V}_I[-\phi]$  of Isink like systems. The correlation functions of this field theory are defined as usual as

$$\begin{aligned} G_{\phi}^{(n)}[B](1, \dots, n) &= \left\langle \prod_{i=1}^n \phi(i) \right\rangle_{\mathcal{H}_{LG}} \\ &= \frac{1}{\Xi_{LG}} \frac{\delta^n \Xi_{LG}[B]}{\delta B(1) \dots \delta B(n)} , \end{aligned} \quad (5.8a)$$

$$G_{\phi,c}^{(n)}[B](1, \dots, n) = \frac{\delta^n \log \Xi_{LG}[B]}{\delta B(1) \dots \delta B(n)} . \quad (5.8b)$$

Since it follows from the definition (5.7) of  $B$  that

$$\frac{\delta}{\delta \nu} = (\beta w)^{-1} * \frac{\delta}{\delta B} , \quad (5.9)$$

we deduce readily from the relation  $\log \Xi[\nu] = \log \Xi_{HS}[\nu_0] + \log \Xi_{LG}[B] - \langle \Delta \nu | (\beta w)^{-1} | \Delta \nu \rangle / 2$  that  $\rho = (\beta w)^{-1} * (\langle \phi | \mathcal{H}_{LG} - \Delta \nu \rangle \equiv (\beta w)^{-1} * \langle \varphi | \mathcal{H}$ , which coincides with relation (2.39c). Performing then  $n$  successive functional derivatives of  $\log \Xi[\nu]$  in taking into account eq. (5.9) one proves easily the following relations

$$G_c^{(2)}[\nu] = -(\beta w)^{-1} + \overline{G}_{\phi,c}^{(2)}[B] \quad (5.10a)$$

$$G_c^{(n)}[\nu] = \overline{G}_{\phi,c}^{(n)}[B] \quad \text{for } n \geq 3 , \quad (5.10b)$$

where

$$\overline{G}_{\phi,c}^{(n)}[B](1, \dots, n) = \int d1' \dots dn' (\beta w)^{-1}(1, 1') \dots (\beta w)^{-1}(n, n') G_{\phi,c}^{(n)}[B](1', \dots, n') . \quad (5.10c)$$

Since the KSSHE fields  $\phi$  and  $\varphi$  differ by a constant  $\Delta\nu$  the connected correlation functions  $G_{\phi,c}^{(n)}[B]$  and  $G_{\varphi,c}^{(n)}[\nu]$  are equal for  $n \geq 2$ . Note that in the case  $n = 2$  eq. (5.10) coincides fortunately with eq. (2.41).

When evaluated for a homogeneous field  $\Phi = cte$  the LG Hamiltonian  $\mathcal{H}_{LG}[\phi] = Vh_{LG}[\phi]$  where  $h_{LG}[\phi]$  takes the familiar form<sup>11,14</sup>

$$h_{LG}[\phi] = \frac{1}{2}r_0\phi^2 - B\phi + \sum_{n=3}^{\infty} u_n\phi^n, \quad (5.11)$$

where  $r_0 = K - K_0$ , with  $K = 1/(\beta\tilde{w}(0))$  proportional to the temperature and  $K_0 = \rho_{HS}^{(1)}(\nu_0)$ . In this case we have simply  $B = \rho_{HS}(\nu_0) + K\Delta\nu$  and finally  $u_n = -\beta P_{HS}^{(n)}(\nu_0) = -\rho_{HS}^{(n-1)}(\nu_0)$ . Note that, in general, odd and even powers of  $\phi$  enter the expression of  $h_{LG}[\phi]$ .

## VI. THE LIQUID-VAPOUR TRANSITION

### A. The mean field KSSHE theory

#### 1. General discussion

We apply the results obtained on the previous sections to discuss now the liquid-vapour transition. The subject was discussed to some extent by Brillantov in ref.<sup>7</sup> with however some inaccuracies that we correct and some missing points that we include in our discussion.

With the notations of section V the MF equations (3.2) take the familiar form

$$\left. \frac{\delta\mathcal{H}_{LG,0}}{\delta\phi} \right|_{\bar{\phi}} = B \equiv \rho_{HS}[\nu_0] + (\beta w)^{-1} * \Delta\nu. \quad (6.1)$$

Eq. (6.1) gives the MF magnetisation of the magnetic system associated to the fluid in the presence of the magnetic field  $B$ . For a homogeneous system we seek a solution  $\phi = \bar{\phi} = cte$  of eq. (6.1). This is equivalent to find the minima of the function  $h(\phi) = h_{LG}(\phi) + K\Delta\nu^2/2 - \beta P_{HS}(\nu_0)$ . We have

$$h(\phi) = \frac{K}{2}\Delta\nu^2 + \frac{K}{2}\phi^2 - K\Delta\nu\phi - \beta P_{HS}(\nu_0 + \phi); \quad (6.2a)$$

$$h'(\phi) = K\phi - K\Delta\nu - \rho_{HS}(\nu_0 + \phi), \quad (6.2b)$$

$$h''(\phi) = K - \rho'_{HS}(\nu_0 + \phi). \quad (6.2c)$$

Moreover the link between the fluid and the associated magnetic system is made through the relation

$$B = \rho_{HS}(\nu_0) + K\Delta\nu. \quad (6.3)$$

Let us first discuss the case  $K > 0 \iff \tilde{w}(0) > 0$ , i.e. when the pair potential is more attractive than repulsive. It is clear from eqs. (6.2) that the convexity of the function  $\beta P_{HS}(\nu)$  governs the properties of the function  $h(\phi)$ . Since  $\beta P_{HS}(\nu)$  is convex its second derivative  $\beta P_{HS}''(\nu) = \rho'_{HS}(\nu)$  is positive for all  $\nu$ . Moreover for all reasonable equation of state of the HS fluid the function  $\beta P_{HS}''(\nu)$  exhibits a unique maximum at some  $\nu_0 = \nu_0^*$  as can be seen in figure (1) where the graphs of some derivatives  $\rho_{HS}^{(n)}(\nu)$  of the HS density are sketched within the framework of the Carnahan-Starling (CS) approximation<sup>1</sup>. In the CS approximation we have  $\nu_0^* = -0.025$  and  $\beta P_{HS}''(\nu_0^*) = K_0 = 0.090$ . Similar values are found in the Percus-Yevick (PY) approximation<sup>1</sup> (via the compressibility route which is simpler, see table I) since, at moderate densities, the predictions of the two theories are in close agreement.

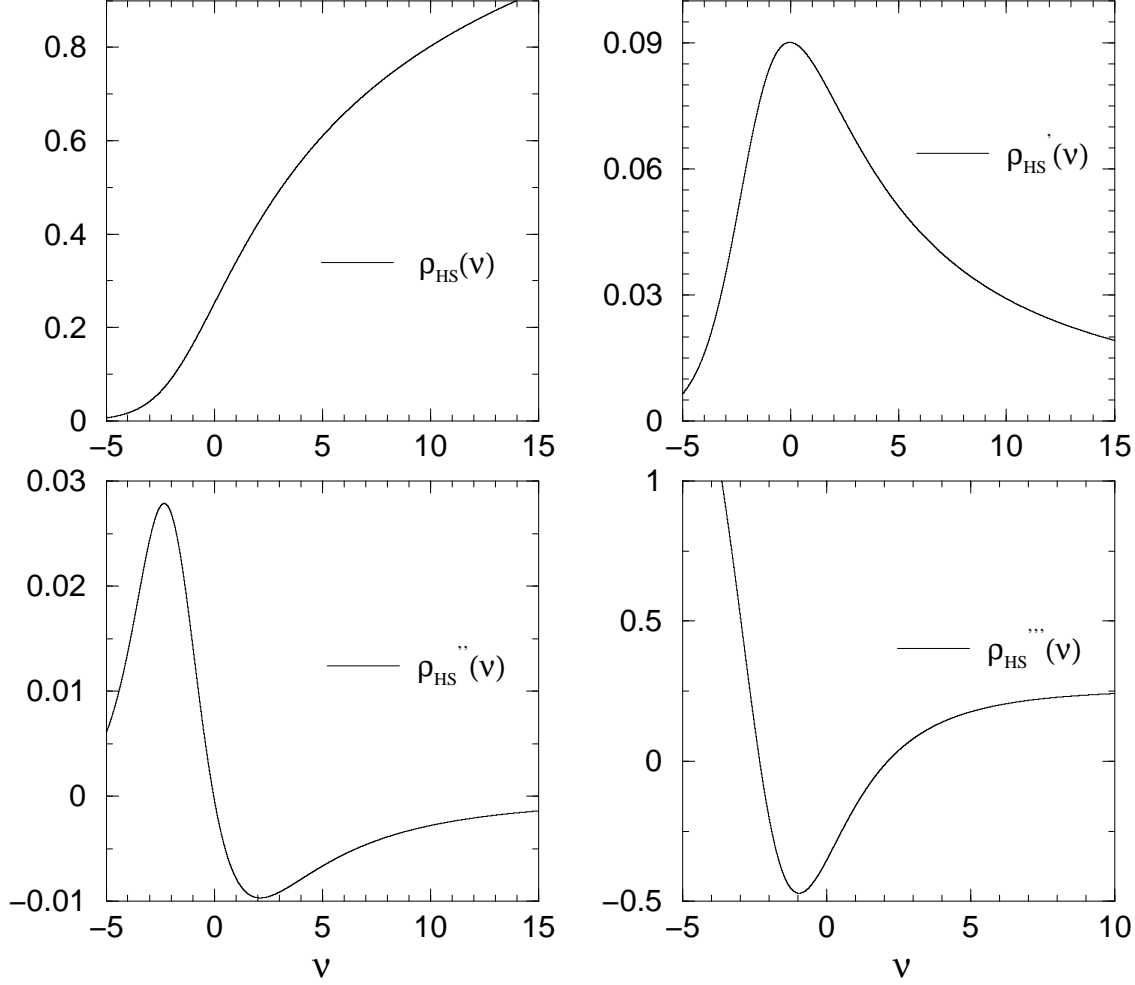


FIG. 1. The HS density  $\rho_{HS}(\nu)$  and its first derivatives  $\rho_{HS}^{(n)}(\nu)$  versus the chemical potential  $\nu$ . The graphs were drawn with the help of a parametric representation  $[\rho_{HS}^{(n)}(\nu) = a(\eta), \nu = b(\eta)]$  ( $\eta$  packing fraction) extracted from the CS equation of state<sup>1</sup>.

Therefore, for  $K > K_0$  we have  $h''(\phi) \geq 0$  for all values of  $\phi$  which implies that  $h(\phi)$  is convex. Since  $\lim_{\phi \rightarrow \pm\infty} h(\phi) = +\infty$  then  $h(\phi)$  has one minimum for some  $\bar{\phi}$  and this minimum is unique.  $\nu_0$  being given, let us choose now  $\nu$  such that  $B = 0$  then it follows from eqs. (6.3) and (6.2b) that the MF equation  $h'(\bar{\phi}) = 0$  can be rewritten as

$$K\bar{\phi} = \rho_{HS}(\nu_0 + \bar{\phi}) - \rho_{HS}(\nu_0). \quad (6.4)$$

A solution of eq. (6.4) is obviously  $\bar{\phi} = 0$  and it is the unique solution, for  $K > K_0$ . For  $K \leq K_0$  the function  $h(\phi)$  is no longer convex and other solutions arise.

Let us assume now that  $K \leq K_0$ . We examine first the case  $\nu_0 = \nu_0^*$ . Noting for convenience  $\phi^*$  the KSSHE field and  $h^*$  the Landau function in this case we have from eq. (5.11)

$$h^*(\phi^*) = \frac{K}{2}\Delta\nu^{*2} + \frac{r_0}{2}\phi^{*2} - B^*\phi^* + \frac{u_4^*}{4!}\phi^{*4} + \mathcal{O}(\phi^{*5}); \quad (6.5a)$$

$$B^* = \rho_{HS}(\nu_0^*) + K\Delta\nu^*, \quad (6.5b)$$

$$\Delta\nu^* = \nu - \nu_S - \nu_0^*, \quad (6.5c)$$

$$u_4^* = -\rho_{HS}^{(3)}(\nu_0^*) > 0. \quad (6.5d)$$



Since  $u_3^* = -\rho_{HS}^{(2)}(\nu_0^*) = 0$  and moreover  $u_4^* \equiv -\rho_{HS}^{(3)}(\nu_0^*) > 0$  (see the table and figure (1)) the Landau function  $h^*(\phi^*)$  describes a 2<sup>nd</sup> order phase transition with a critical point at  $(B^* = 0, K = K_0)$ . For  $K \leq K_0$  and  $B^* = 0$  the solution  $\bar{\phi} = 0$  of eq. (6.4) becomes unstable and two stable solutions  $\pm\bar{\phi}_0 \neq 0$  corresponding to a liquid and a vapour phase emerge.

Now if  $\nu_0 \neq \nu_0^*$  a term in  $\phi^3$  is present in the Landau function  $h(\phi)$  at  $B = 0$  which describes now a first order transition without critical point. This apparent paradox is solved in the next section. A sketch of the functions  $h^*(\phi^*)$  and  $h(\phi)$  is given in figure (2) to illustrate our discussion.

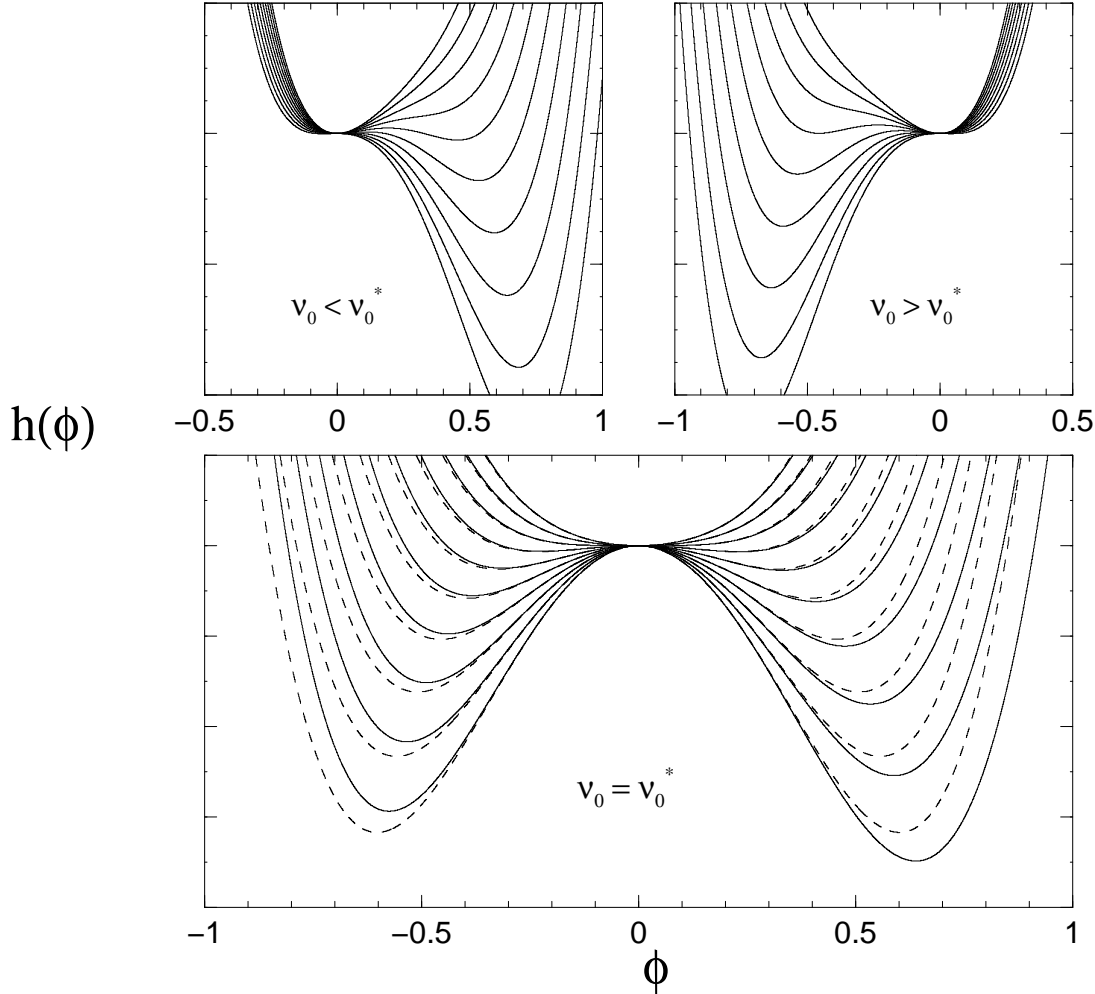


FIG. 2. The Landau-Ginzburg Hamiltonian  $h(\phi)$  in zero field ( $B = 0$ ) for various choices of the reference chemical potential  $\nu_0$  and for different temperatures  $K$  in the vicinity of  $K_c$ . In each bunch of curves  $K$  increases from bottom to top.  $h(\phi)$  was computed in the CS approximation. Only the choice  $\nu_0 = \nu_0^*$  yields a second order phase transition with a critical point (bottom curve). In this case the dashed symmetric curves were obtained by truncating  $h(\phi)$  at the order  $\phi^4$  (included). For  $\nu_0 \neq \nu_0^*$ ,  $h(\phi)$  describes a first order phase transition (top curves) without critical point. The units of  $h(\phi)$  were not specified for more clarity.

Let us now consider briefly the case  $K < 0$  of a repulsive tail. In this case  $h^{(2)}(\phi)$  is negative for all  $\phi$  and the function  $h(\phi)$ ,  $\phi \in \mathbb{R}$  is concave with a unique *maximum* for some  $\bar{\phi}$ . For  $\phi$  assuming imaginary values  $h(\bar{\phi})$  is obviously a minimum of  $h(\phi)$  and the point  $(\bar{\phi}, h(\bar{\phi}))$  is indeed a saddle point. Therefore for  $K < 0$  no transition occurs, at least at the MF level. Henceforth we shall assume that  $K > 0$ .

## 2. The Hubbard-Schofield transform and the critical point

When we make choice of the special value  $\nu_0 = \nu_0^*$  the Landau function has the following exact expression

$$h^*(\phi^*) = \frac{K}{2} \Delta \nu^{*2} + \frac{1}{2} \phi^{*2} - K \Delta \nu^* \phi^* - \beta P_{HS}(\nu_0^* + \phi^*) , \quad (6.6)$$

where we have kept the notations of section (VI A 1). A Taylor expansion of eq. (6.6) around  $\phi^* = 0$  gives back the usual ferromagnetic LG Hamiltonian (6.5a) with no term in  $\phi^{*3}$ . The following set of transformations

$$\phi = \phi^* + \nu_0^* - \nu_0 , \quad (6.7a)$$

$$\Delta \nu = \Delta \nu^* + \nu_0^* - \nu_0 , \quad (6.7b)$$

obviously enables us to write  $h(\phi) \equiv h^*(\phi^*)$  where  $h(\phi)$  is given precisely by eq. (6.2a). The relations (6.7) constitute the exact Hubbard-Schofield transformation which allows to get rid of the term in  $\phi^3$  in  $h(\phi)$ <sup>5</sup>. Note that under this transformation

$$B = B^* + K(\nu_0^* - \nu_0) + \rho_{HS}(\nu_0) - \rho_{HS}(\nu_0^*) , \quad (6.8)$$

as can be inferred readily from the definition (6.3) of the magnetic field  $B$ . As a consequence, the function  $h(\phi)$  at zero field which describes a system undergoing a *first order phase transition* may be seen as the LG Hamiltonian associated with a system undergoing a *second order phase transition* in presence of the field  $B^* = -K(\nu_0^* - \nu_0) - \rho_{HS}(\nu_0) + \rho_{HS}(\nu_0^*)$ .

Henceforth we shall adopt for definiteness the choice  $\nu_0 = \nu_0^*$  and drop all the subscripts “\*” to simplify the notations. With this choice, the liquid is associated with a magnetic system with magnetisation  $\phi$  and the liquid-vapour transition and its critical point can be made in a one to one correspondance with the para-ferromagnetic (second order) transition and its critical point. Since the magnetisation and the density of the fluid are equal (up to a multiplicative constant) the order parameter of the liquid-vapour transition is merely the density. The field-mixing hypothesis of Rehr and Mermin<sup>17,18</sup> is therefore meaningless in the present theory.

The MF critical point of the liquid-vapour transition is therefore defined by the conditions

$$K_c = K_0 , \quad (6.9a)$$

$$\bar{\phi}_c = 0 , \quad (6.9b)$$

$$B_c = 0 . \quad (6.9c)$$

The first condition (6.9a) can be satisfied only if  $\tilde{w}(0) \equiv (\tilde{w}_-(0) - \tilde{w}_+(0)) > 0$ , i.e. if the pair potential is more attractive than repulsive.  $K_c = \rho_{HS}^{(1)}(\nu_0) \sim 0.290$  (see the table) is a universal quantity in the sense that it does not depend on the pair potential, however the critical temperature  $T_c = K_c/\tilde{w}(0)$  is not universal and depends in particular upon the regularisation of  $w(r)$  in the core. The second condition (6.9b) determines the critical density since it follows from (3.6) that  $\rho_c = \rho_{HS}(\nu_0) \sim 0.249$  (see the table).  $\rho_c$  is therefore also a universal quantity. Finally the third condition (6.9c) determines the critical chemical potential  $\Delta \nu_c = -\rho_{HS}(\nu_0)/\rho_{HS}^{(1)}(\nu_0)$ .  $\Delta \nu_c$  is universal but not  $\nu_c$  which once again depends upon  $w$  and its regularisation.

All the conclusions concerning the universality of some of the critical parameters in the MF approximation originate in our choice of treating at the same level the attractive and the repulsive part of the pair interaction. If the repulsive part  $w_+$  is treated exactly and included in the reference system then  $\rho_c$ ,  $K_c$ , and  $\Delta \nu_c$  are no longer universal quantities.

In ref.<sup>7</sup> an approximate Hubbard-Schofield transformation was devised by considering the truncated Taylor expansion of  $h(\phi)$  rather than its exact expression (6.2a); it yields  $\rho_c \neq \rho_{HS}(\nu_0)$  and that  $\rho_c$  can moreover be adjusted at will to fit with experimental or numerical simulation results; these two conclusions are however incorrect.

## 3. Mean Field solution for $T > T_c$

We have seen in section (VI A 1) that for  $K > K_c \equiv \rho_{HS}^{(1)}(\nu_0)$ , the MF solution  $\bar{\phi}$  is unique and satisfies the relation

$$h'(\bar{\phi}) = 0 \iff K\bar{\phi} = K\Delta \nu + \rho_{HS}(\nu_0 + \bar{\phi}) . \quad (6.10)$$

The general results of section (III) can be specialised to the uniform case and yield

$$\beta P_{MF}(\nu) = \beta P_{HS}(\nu_0 + \bar{\phi}) - \frac{1}{2K} \rho_{HS}^2(\nu_0 + \bar{\phi}) , \quad (6.11a)$$

$$\rho_{MF}(\nu) = \rho_{HS}(\nu_0 + \bar{\phi}) , \quad (6.11b)$$

$$\beta f_{MF}(\rho) = \beta f_{HS}(\rho) - \frac{\rho^2}{2} \beta \tilde{w}(0) + \frac{\rho}{2} \beta w(0) . \quad (6.11c)$$

Note that the critical pressure

$$\beta P_c = \beta P_{HS}(\nu_0) - \frac{\rho_{HS}^2(\nu_0)}{2\rho_{HS}^{(1)}(\nu_0)} \quad (6.12)$$

is a universal quantity (one finds for the critical compressibility factor  $Z_c = \beta P_c / \rho_c \sim 0.3589(CS)$  ,  $0.3598(PYC)$ ). Note also that eq. (6.11b) implies that the critical isochore  $\rho = \rho_c$  is defined by the condition  $B = 0$ , since in the case the (unique) solution of (6.10) is  $\bar{\phi} = 0$ .

We complete the above results by establishing now the MF expressions for the internal energy, the specific heat and the compressibility. The excess internal energy by unit of volume  $u_{ex}$  is given by

$$\begin{aligned} u_{ex}(\rho, \beta) &= \frac{\partial}{\partial \beta} [\beta f_{MF}(\rho) - \beta f_{HS}(\rho)] , \\ &= \frac{\rho}{2} w(0) - \frac{\rho^2}{2} \tilde{w}(0) , \end{aligned} \quad (6.13)$$

from which it follows that in the MF approximation the excess specific heat vanishes above  $T_c$  :

$$C_{V,ex} = \left. \frac{\partial u_{ex}}{\partial \beta} \right|_{\rho} \equiv 0 . \quad (6.14)$$

The isothermal compressibility  $\chi_T = \beta \rho^{-2} (\partial \rho / \partial \nu)_{\beta}$  can be rewritten as

$$\chi_T = \frac{\beta}{\rho_{HS}^2(\nu_0 + \bar{\phi})} \rho_{HS}^{(1)}(\nu_0 + \bar{\phi}) \left. \frac{\partial \bar{\phi}}{\partial \nu} \right|_{\beta} . \quad (6.15)$$

For it follows from the MF equation (6.10) that

$$\left. \frac{\partial \bar{\phi}}{\partial \nu} \right|_{\beta} = \frac{K}{K - \rho_{HS}^{(1)}(\nu_0 + \bar{\phi})} \quad (6.16)$$

we have finally

$$\chi_T = \frac{\beta}{\rho_{HS}^2(\nu_0 + \bar{\phi})} \frac{K \rho_{HS}^{(1)}(\nu_0 + \bar{\phi})}{K - \rho_{HS}^{(1)}(\nu_0 + \bar{\phi})} . \quad (6.17)$$

Alternatively,  $\chi_T$  could have been obtained from the Fourier transform at  $k = 0$  of the two-body correlation function, by making use of a well-known expression of the theory of liquids<sup>1</sup>

$$\begin{aligned} \chi_T &= \frac{\beta}{\rho_{HS}^2(\nu_0 + \bar{\phi})} \tilde{G}_{MF,c}[\nu](k=0) , \\ &= \frac{\beta}{\rho_{HS}^2(\nu_0 + \bar{\phi})} \frac{\tilde{G}_{HS,c}^{(2)}[\nu_0 + \bar{\phi}](0)}{1 - K^{-1} \tilde{G}_{HS,c}^{(2)}[\nu_0 + \bar{\phi}](0)} , \end{aligned} \quad (6.18)$$

where we made use of eq. (3.28). Noting that  $\tilde{G}_{HS,c}^{(2)}[\nu_0 + \bar{\phi}](0) = \rho_{HS}^{(1)}(\nu_0 + \bar{\phi})$  we are led back to eq. (6.17). Along the critical isochore ( $\rho = \rho_c \iff \bar{\phi} = 0$ ) one has simply

$$\chi_T(\rho_c) = \frac{\beta}{\rho_c^2} \frac{K_c}{K - K_c} , \quad (6.19)$$

with a divergence for  $K \rightarrow K_c +$  with a MF critical exponent  $\gamma = 1$  as expected.

The behavior of  $\tilde{G}_{MF,c}(k)$  for  $k \rightarrow 0$  along the critical isochore is also easy to study. As a consequence of eqs. (2.31) and (3.28) one has

$$\tilde{G}_{MF,c}[\rho_c](k) = \frac{\rho_c}{1 - \rho_c(\tilde{c}_{HS}[\rho_c](k) + \beta\tilde{w}(k))} , \quad (6.20)$$

where  $\tilde{c}_{HS}[\rho_c](k)$  is the Fourier transform of the usual direct correlation function of the HS fluid at the density  $\rho_c = \rho_{HS}(\nu_0)$ . At low  $k$ 's one has

$$\begin{aligned} \tilde{c}_{HS}[\rho_c](k) + \beta\tilde{w}(k) &= \tilde{c}_{HS}[\rho_c](0) + \beta\tilde{w}(0) - ak^2 + \mathcal{O}(k^4) , \\ a &= \frac{-1}{2}[\beta\tilde{w}^{(2)}(0) + \tilde{c}_{HS}^{(2)}[\rho_c](0)] , \end{aligned} \quad (6.21)$$

which implies, putting all things together and after having noted that  $1 - \rho_c\tilde{c}_{HS}[\rho_c](0) = \rho_c/K_0$  that

$$\tilde{G}_{MF,c}[\rho_c](k) \sim \frac{KK_0}{K - K_0} \frac{1}{1 + \xi^2 k^2} \quad \text{for } k \rightarrow 0 , \quad (6.22)$$

where the correlation length  $\xi$  reads as

$$\xi = \frac{a^{1/2}}{(K - K_0)^{1/2}} . \quad (6.23)$$

Of course  $\xi$  is defined only if  $a > 0$  which put some restrictions on the pair potential (cf eq. (6.21) and note that  $\tilde{c}_{HS}^{(2)}[\rho_c](0) \sim 1.331$  (PYC) ).  $\xi$  diverges for  $K \rightarrow K_c+$  along the critical isochore with, as expected, a MF exponent  $\nu = 1/2$ . At the critical temperature eq. (6.22) implies that  $\tilde{G}_{MF,c}(k) \sim k^{-2}$  the usual behavior in the MF approximation yielding  $\eta = 0$  for the Fisher exponent.

We end this section by a discussion of the behaviour of the order parameter along the critical isotherm  $K = K_c$ . Near the critical point the MF eq. (VIA 3) at  $T_c$  can be reexpressed as

$$\begin{aligned} \bar{\phi} &= \Delta\nu + \frac{\rho_{HS}(\nu_0 + \bar{\phi})}{\rho_{HS}^{(1)}(\nu_0)} , \\ &= \Delta\nu - \Delta\nu_c + \bar{\phi} + \frac{1}{3!} \frac{\rho_{HS}^{(3)}(\nu_0)}{\rho_{HS}^{(1)}(\nu_0)} \bar{\phi}^3 + \mathcal{O}(\bar{\phi}^4) , \end{aligned} \quad (6.24)$$

yielding

$$\bar{\phi}^3 = \frac{6}{u_4}(\nu - \nu_c)\rho_{HS}^{(1)}(\nu_0) . \quad (6.25)$$

Therefore along the critical isotherm we have finally

$$\rho = \rho_{HS}(\nu_0 + \bar{\phi}) \sim \rho_{HS}(\nu_0) + \rho_{HS}^{(1)}(\nu_0)^{4/3}(6/u_4)^{1/3}(\nu - \nu_c)^{1/3} \quad (6.26)$$

yielding the classical value  $\delta = 3$  of the critical exponent, as expected.

#### 4. Mean Field solution for $T < T_c$

Below (and near)  $T_c$  it is sufficient to consider the truncated expansion (6.2) of the Landau function  $h(\phi)$ . The solution of the MF equation is of course well known in this case. Let us define  $\hat{B} = B/|B|$ . Besides  $\bar{\phi} = 0$ , the MF equations  $h^{(1)}(\phi) = 0$  have the solution<sup>11,12,14</sup>

$$\begin{aligned} \bar{\phi} &= \bar{\phi}_0 \hat{B} + \delta\bar{\phi} , \\ \bar{\phi}_0 &= \left( \frac{3!}{u_4} \right)^{1/2} (K_0 - K)^{1/2} , \\ \delta\bar{\phi} &= \frac{B}{2(K - K_0)} + \mathcal{O}(B^2) . \end{aligned} \quad (6.27)$$

In zero field (i.e.  $B = 0$ ) the solution  $\bar{\phi} = 0$  is unstable and the two solutions  $\bar{\phi} = \pm|\bar{\phi}_0|$  are stable. The densities corresponding to the magnetisations  $\pm|\bar{\phi}_0|$  are those of the coexisting liquid and vapour; they are given by

$$\begin{aligned}\rho_{l,g} &= \rho_{HS}(\nu_0 \pm |\bar{\phi}_0|), \\ &\sim \rho_{HS}(\nu_0) \pm \rho_{HS}^{(1)}(\nu_0) \left(\frac{3!}{u_4}\right)^{1/2} (K_0 - K)^{1/2},\end{aligned}\quad (6.28)$$

yielding a value  $\beta = 1/2$  for the exponent of the order parameter, as expected. It can be noticed that eq. (6.28) supports the law of rectiligned diameters with the simple result (valid in the vicinity of  $T_c$ )  $\rho_l + \rho_g = 2 \times \rho_c$ . The chemical potential at the coexistence is given by  $\Delta\nu_{coex} = -\rho_{HS}(\nu_0)/K$  as a consequence of the condition  $B = 0$  and the pressure at coexistence reads as

$$\beta P_{coex} = \beta P_{HS}(\nu_0) - \frac{\rho_c^2}{2K} + \frac{3}{2u_4}(K - K_0)^2 \quad (6.29)$$

Therefore  $\nu_{coex}$  and  $\beta P_{coex}$  are both regular functions of the temperature  $K$  near  $K_c$ .

The compressibility is not defined in the two phases region but one can compute the excess specific heat at constant volume thanks to a formula due to Yang and Yang<sup>25</sup>. Along the critical isochore one has

$$C_{V,ex} = T \frac{\partial^2 P_{coex}}{\partial T^2} - \rho_c T \frac{\partial^2 \mu_{coex}}{\partial T^2}, \quad (6.30)$$

which yields after some algebra to

$$C_{V,ex} = \frac{3\rho_{HS}^{(1)}(\nu_0)^2}{2u_4}. \quad (6.31)$$

The comparison of eqs. (6.14) and (6.31) show that the specific heat at  $\rho_c$  has a discontinuity of universal value  $\Delta C_{V,ex} \sim 3\rho_{HS}^{(1)}(\nu_0)^2/2u_4 \sim 1.0496$  (CS) or 1.0074 (PYC), yielding a MF value  $\alpha = 0$  for the critical exponent of  $C_{V,ex}$  as expected.

### 5. The Gaussian approximation

As well known, the critical exponents of the Gaussian model are the same as those of the MF theory except  $\alpha$ . We shall thus content ourselves to compute  $C_{V,ex}$  along the critical isochore above  $T_c$ . Since  $C_{V,ex}(\rho_c)$  vanishes in the MF approximation above  $T_c$ , it is equal to  $(\partial^2 \beta \Delta f / \partial \beta^2)_{\rho_c}$  in the Gaussian approximation where  $\beta \Delta f$  has been defined in eq. (4.14c). Working out the derivatives one find that

$$C_{V,ex}(\rho_c) = \frac{1}{2} \int \frac{d^3 \vec{k}}{(2\pi)^3} \left[ \tilde{G}_{MF,c}^{(2)}[\rho_c](k) \beta \tilde{w}(k) \right]^2. \quad (6.32)$$

The integral diverges in the limit  $K \rightarrow K_c+$  because of the singular behavior of  $\tilde{G}_{MF,c}^{(2)}[\rho_c](k)$  at small  $k$ 's. The method for extracting the divergence of  $C_{V,ex}(\rho_c)$  is well documented<sup>11,12,14</sup> and will not be repeated here. The idea is to make the change of variable  $\vec{k}' = \xi \vec{k}$ , where  $\xi$  is the correlation length and to inject in eq. (6.32) the small "k" behaviour of  $\tilde{G}_{HS,c}^{(2)}[\rho_c](k)$  as given by eq. (6.22). One finds for  $K \rightarrow K_c+$

$$C_{V,ex}(\rho_c) \sim \frac{\rho_{HS}^{(1)}(\nu_0)^2}{16\pi a^{3/2}} (K - K_c)^{-1/2}, \quad (6.33)$$

yielding a divergence in  $t^{-1/2}$  as expected. Below  $T_c$  a similar behavior (with a different prefactor) can be obtained by making use of the Yang-Yang formula. As well known, a comparison of the discontinuity  $\Delta C_{V,ex}(\rho_c)$  of the specific heat in the MF approximation (cf eq. (6.31)) and its Gaussian behavior (6.33) allows an estimate of the Ginzburg temperature range  $\Delta K$ , in our case one has  $\Delta K \sim a^{3/2}/u_4$ . It depends on the pair potential  $w$  through the parameter  $a$  defined at eq. (6.21). Since  $a \sim 1$  and  $u_4$  is tiny in general,  $\Delta K/K_c > 1$ .

## VII. CONCLUSION

In this paper we have presented an exact field theoretical representation of the statistical mechanics of a simple model of liquid. The action of the theory is obtained with the help of a KSSHE transform of the Boltzman factor of the fluid. Some complications of the formalism such that the fact that the action of the KSSHE theory is not a local functional of the field have their origin in the necessity to take an explicit account of the hard core interactions. However, it is possible to establish the relations between the correlation functions of the field and that of the density of the fluid. Moreover the KSSHE action can be interpreted as the Landau-Ginzburg action of a ferromagnetic system in the presence of a magnetic field  $B$  which is related linearly with the local chemical potential of the liquid.

The MF and Gaussian approximation of the KSSHE theory can be worked out explicitly. For homogeneous fluids the Gaussian approximation coincides with the RPA theory. These two approximations yield a rough description of the liquid-vapour transition. The exact Hubbard-Schofield transformation can be established which yields the usual LG Hamiltonian in  $\phi^4$  of the theory of critical phenomena. The density emerges as the order parameter of the transition which rules out the field mixing hypothesis. The critical density turns out to be independant from the details of the attractive part of the potential which is a serious flaw. Moreover several critical properties either do not depend on the potential  $w(r)$  or depend strongly on the regularisation of  $w(r)$  in the core which is in both cases unsatisfactory. By lack of place we did not discuss the full one-loop order theory where fresh difficulties arise such as unavoidable corrections to the magnetic field  $B$ , the order parameter, and more generally all the correlation functions. A fully renormalized theory at the one-loop order seems however feasible despite these difficulties.

The MF-KSSHE theory also works for inhomogeneous fluids and yields density functionals which could be usefull in applications. Moreover for two classes of pair potentials, the MF-KSSHE free energy functional constitutes a rigorous bound for the exact free energy functional which could serve as a test in numerical studies. A similar result holds also for the grand-potential functional above the critical point.

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## APPENDIX A: FUNCTIONAL INTEGRATION

In the case where the domain occupied by the particles of the fluid is a cube of side  $L$  with periodic boundary conditions (  $\Omega \equiv \mathcal{C}_3$  ) we give an explicit expression of the measure  $\mathcal{D}\varphi$  which enters the functional integrals considered in this paper.

In cubico-periodical geometries the microscopic density  $\hat{\rho}$  can be written as a Fourier series

$$\begin{aligned}\hat{\rho}(\vec{r}) &= \frac{1}{L^3} \sum_{\vec{k} \in \Lambda} \hat{\rho}_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) , \\ \hat{\rho}_{\vec{k}} &= \sum_{i=1}^N \exp(-i\vec{k} \cdot \vec{r}_i) ,\end{aligned}\tag{A1}$$

where  $\Lambda = (2\pi/L) \mathbb{Z}^3$  denotes the reciprocal lattice. Note that since  $\hat{\rho}$  is real one has

$$\hat{\rho}_{\vec{k}} = \hat{\rho}_{-\vec{k}}^* .\tag{A2}$$

The pair potentials  $w_{\pm}^{\mathcal{C}_3}(\vec{r}_{ij})$  between two particles  $i$  and  $j$  must take into account the interactions between the periodical images of  $i$  and  $j$ . They are both periodical functions of  $\vec{r}_{ij}$  which can be written as<sup>1</sup>

$$w_{\pm}^{\mathcal{C}_3}(\vec{r}) = \sum_{\vec{n} \in \mathbb{Z}^3} w_{\pm}(\vec{r} + L\vec{n}) ,\tag{A3}$$

The above expression for  $w_{\pm}^{\mathcal{C}_3}(\vec{r})$  can also be written as a Fourier series, the Fourier coefficients of which are precisely the Fourier transforms of  $w_{\pm}(r)$  as a consequence of Poisson's formula. Therefore one also has

$$w_{\pm}^{C^3}(\vec{r}) = \frac{1}{L^3} \sum_{\vec{k} \in \Lambda} \tilde{w}_{\pm}(k) \exp(i\vec{k} \cdot \vec{r}) . \quad (\text{A4})$$

where  $\tilde{w}_{\pm}(k)$  is real and has been defined at eq. (2.1). It follows from eqs (A1) and (A3) that, in  $C^3$ , the potential energies  $\langle \hat{\rho}^{C^3} | w_{\pm}^{C^3} | \hat{\rho}^{C^3} \rangle$  in  $C^3$  can be reexpressed as

$$\frac{1}{2} \langle \hat{\rho}^{C^3} | w_{\pm}^{C^3} | \hat{\rho}^{C^3} \rangle = \frac{1}{L^3} \sum_{\vec{k} \in \Lambda^*} \tilde{w}_{\pm}(k) |\hat{\rho}_{\vec{k}}|^2 , \quad (\text{A5})$$

where the sum in the r.h.s runs over only the half  $\Lambda^*$  of all the vectors of the reciprocal lattice  $\Lambda$  (for instance those with  $n_x \geq 0$ ) as a consequence of the reality of  $\tilde{w}_{\pm}(k)$  and of the symetry relations (A2).

At this point we introduce a periodic real field  $\varphi(\vec{r})$  supposed to be expressible as a Fourier series

$$\varphi(\vec{r}) = \frac{1}{L^3} \sum_{\vec{k} \in \Lambda} \tilde{\varphi}(\vec{k}) \exp(i\vec{k} \cdot \vec{r}) , \quad (\text{A6})$$

and define the measure<sup>14</sup>

$$\begin{aligned} \mathcal{D}\varphi &\equiv \prod_{\vec{k} \in \Lambda^*} d^2 \tilde{\varphi}(\vec{k}) , \\ d^2 \tilde{\varphi}(\vec{k}) &= d \Re \tilde{\varphi}(\vec{k}) d \Im \tilde{\varphi}(\vec{k}) , \end{aligned} \quad (\text{A7})$$

where it is understood that the domain of integration of both the real and imaginary parts of  $\tilde{\varphi}(\vec{k})$  is the whole real axis  $]-\infty, +\infty[$ .

Defining formally

$$\begin{aligned} \langle \varphi | (\beta w_{\pm}^{C^3})^{-1} | \varphi \rangle &= \frac{1}{L^3} \sum_{\vec{k} \in \Lambda} \frac{1}{\beta \tilde{w}_{\pm}(k)} |\tilde{\varphi}(\vec{k})|^2 , \\ &= \frac{1}{L^3} \sum_{\vec{k} \in \Lambda} \frac{1}{\beta \tilde{w}_{\pm}(k)} \left( \Re \tilde{\varphi}(\vec{k})^2 + \Im \tilde{\varphi}(\vec{k})^2 \right) , \end{aligned} \quad (\text{A8})$$

and noting that

$$\langle \hat{\rho} | \varphi \rangle = \frac{2}{L^3} \sum_{\vec{k} \in \Lambda^*} \left( \Re \tilde{\varphi}(\vec{k}) \Re \hat{\rho}_{\vec{k}} + \Im \tilde{\varphi}(\vec{k}) \Im \hat{\rho}_{\vec{k}} \right) , \quad (\text{A9})$$

one deduces easily from the definition (A7) and from properties of ordinary Gaussian integrals

$$\int_{-\infty}^{+\infty} dx \exp\left(-\frac{1}{2}Ax^2 + iJx\right) = (2\pi/A)^{1/2} \exp\left(-\frac{1}{2}A^{-1}J^2\right) (A > 0) , \quad (\text{A10})$$

the fundamental relations

$$\begin{aligned} \exp\left(\frac{1}{2} \langle \hat{\rho} | \beta w_{-}^{C^3} | \hat{\rho} \rangle\right) &= \frac{\int \mathcal{D}\varphi \exp\left(-\frac{1}{2} \langle \varphi | (\beta w_{-}^{C^3})^{-1} | \varphi \rangle + \langle \hat{\rho} | \varphi \rangle\right)}{\int \mathcal{D}\varphi \exp\left(-\frac{1}{2} \langle \varphi | (\beta w_{-}^{C^3})^{-1} | \varphi \rangle\right)} \equiv \langle \exp(\langle \hat{\rho} | \varphi \rangle) \rangle_{\beta w_{-}^{C^3}} , \\ \exp\left(-\frac{1}{2} \langle \hat{\rho} | \beta w_{+}^{C^3} | \hat{\rho} \rangle\right) &= \frac{\int \mathcal{D}\varphi \exp\left(-\frac{1}{2} \langle \varphi | (\beta w_{+}^{C^3})^{-1} | \varphi \rangle + i \langle \hat{\rho} | \varphi \rangle\right)}{\int \mathcal{D}\varphi \exp\left(-\frac{1}{2} \langle \varphi | (\beta w_{+}^{C^3})^{-1} | \varphi \rangle\right)} \equiv \langle \exp(i \langle \hat{\rho} | \varphi \rangle) \rangle_{\beta w_{+}^{C^3}} , \end{aligned} \quad (\text{A11})$$

already mentioned in the main text (cf eqs. (2.5)) with less awkward notations. An important result concerns the ratio of two Gaussian partition functions. Let  $\mathcal{N}_f$  be the constant

$$\mathcal{N}_f \equiv \int \mathcal{D}\varphi \exp\left(-\frac{1}{2} \langle \varphi | f^{-1} | \varphi \rangle\right) , \quad (\text{A12})$$

where  $f$  is some positive two-body operator. Then, for  $f$  and  $g$  positive we have

$$\begin{aligned}\mathcal{N}_f/\mathcal{N}_g &= \prod_{\vec{k} \in \Lambda^*} \frac{\tilde{f}(\vec{k})}{\tilde{g}(\vec{k})}, \\ &\sim \exp \left( \frac{V}{2} \int \frac{d^3 \vec{k}}{(2\pi)^3} \log \frac{\tilde{f}(\vec{k})}{\tilde{g}(\vec{k})} \right);.\end{aligned}\tag{A13}$$

In practice only functional integrals of Gaussian functionals and their derivatives can be performed explicitly. All the feasible integrals can be deduced from Wick's theorem<sup>11–13</sup> which states that

$$\langle \varphi(1) \dots \varphi(2n) \rangle_y = \sum y(i_1, i_2) \dots y(i_{2n-1}, i_{2n}), \tag{A14}$$

where the summation runs over all the  $(2n-1)!!$  distinct pairs  $(i_1, i_2)$ .

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TABLE I. Derivatives of the HS pressure at the chemical potential  $\nu_0$  where  $\beta P_{HS}^{(2)}$  reaches its maximum. The numerical estimates were obtained in the framework of the CS and PYC approximations.

	<i>CS</i>	<i>PYC</i>
$\nu_0$	-0.025	-0.059
$\beta P_{HS}(\nu_0)$	0.433	0.425
$\rho_{HS}(\nu_0) \equiv \beta P_{HS}^{(1)}(\nu_0)$	0.249	0.246
$\rho_{HS}^{(1)}(\nu_0)$	0.090	0.0896
$\rho_{HS}^{(2)}(\nu_0)$	0.0	0.0
$u^4 \equiv -\rho_{HS}^{(3)}(\nu_0)$	0.0116	0.0119
$\Delta\nu_c \equiv -\rho_{HS}(\nu_0)/\rho_{HS}^{(1)}(\nu_0)$	-2.766	-2.743